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THE COST OF CLEAN WATER. VOLUME III. PETROLEUM REFINING

Federal Water Pollution Control Administration
Washington, D.C.

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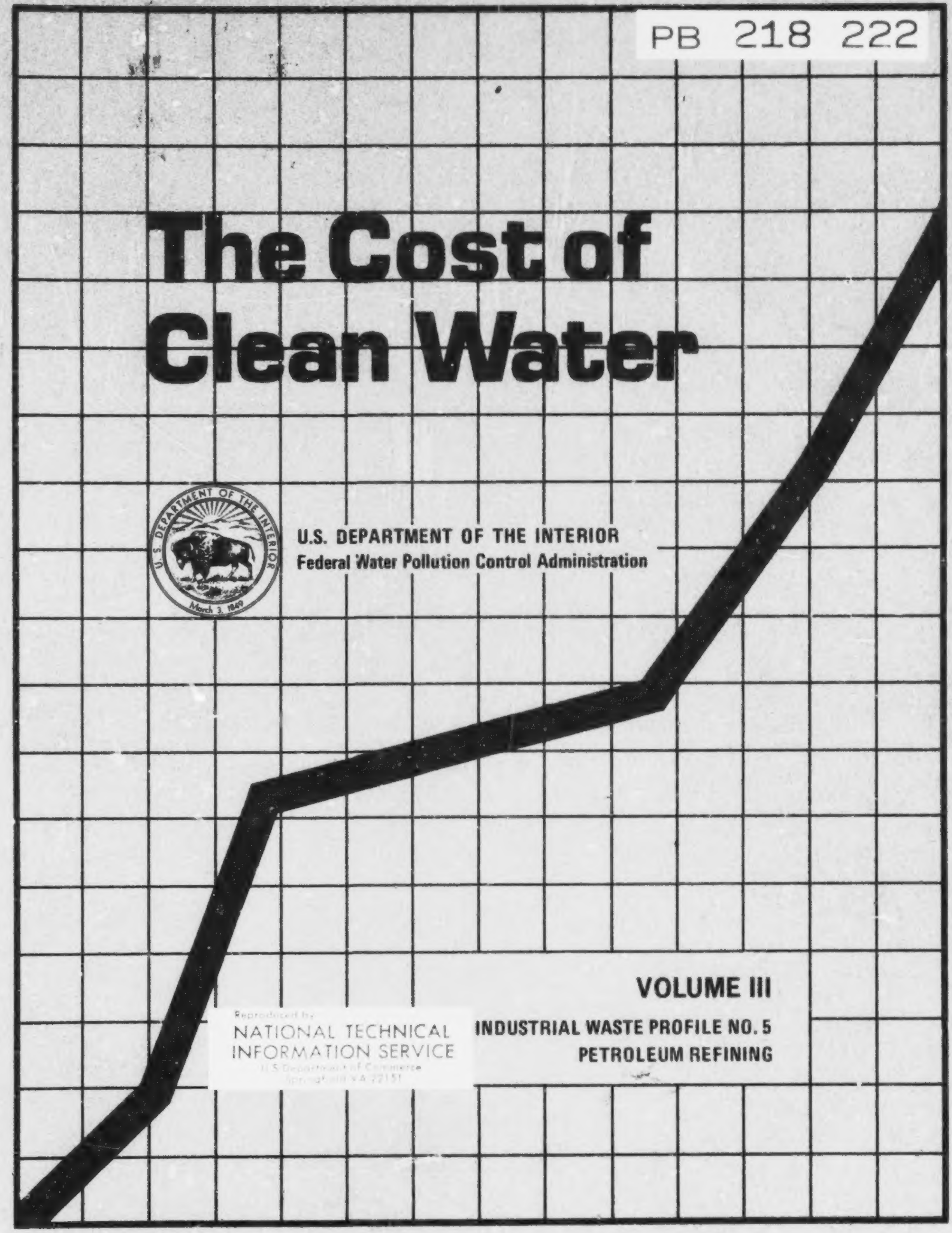

The Cost of Clean Water

March 3, 1849

U.S. DEPARTMENT OF THE INTERIOR
Federal Water Pollution Control Administration

VOLUME III

INDUSTRIAL WASTE PROFILE NO. 5
PETROLEUM REFINING

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THE COST OF
CLEAN WATER

Volume III

Industrial Waste Profiles
No. 5 - Petroleum Refining

U. S. Department of the Interior
Federal Water Pollution Control Administration

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PREFACE

The Industrial Waste Profiles are part of the National Requirements and Cost Estimate Study required by the Federal Water Pollution Control Act as amended. The Act requires a comprehensive analysis of the requirement and costs of treating municipal and industrial wastes and other effluents to attain prescribed water quality standards.

The Industrial Waste Profiles were established to describe the source and quantity of pollutants produced by each of the ten industries studied. The profiles were designed to provide industry and government with information on the costs and alternatives involved in dealing effectively with the industrial water pollution problem. They include descriptions of the costs and effectiveness of alternative methods of reducing liquid wastes by changing processing methods, by intensifying use of various treatment methods, and by increasing utilization of wastes in by-products or water reuse in processing. They also describe past and projected changes in processing and treatment methods.

The information provided by the profiles cannot possibly reflect the cost or wasteload situation for a given plant. However, it is hoped that the profiles, by providing a generalized framework for analyzing individual plant situations, will stimulate industry's efforts to find more efficient ways to reduce wastes than are generally practiced today.

James M. Quigley
Commissioner
Federal Water Pollution Control Administration

PETROLEUM REFINING
INDUSTRY WASTEWATER PROFILE

Prepared for F.W.P.C.A.

F.W.P.C.A. Contract 14-12-100
June 30, 1967

Federal Water Pollution Control Administration
November 1967

SCOPE OF MATERIAL COVERED

This industrial wastewater profile covers the Petroleum Refinery industry in the United States as defined by Standard Industrial Classification 2911 of the U. S. Department of Commerce. It does not cover the production of crude oil or natural gas from wells or the natural gasoline and other operations associated with such production. Transportation of petroleum products is covered only to the extent that it is a part of refinery pollution control, such as treatment of ballast water. The principal areas of discussion are: the fundamental manufacturing processes and their patterns of use, water use and reuse, waste quantities and characteristics, waste reduction practices (including both waste treatment and in-plant processing) and their effectiveness, and waste treatment costs. In each area of discussion trends have been projected to or estimates made for the situation expected in 1977.

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SUMMARY

Introduction

Petroleum Refining is one of the most important manufacturing industries in the country. In 1963 it employed approximately 120,000 people with an annual payroll of about 16 billion dollars. In the same year it accounted for almost 3 percent of the Gross National Product. It is one of the largest "wet" processing industries in the United States. Extensive work has been done in pollution abatement, as indicated by the 1966 estimated replacement value of U. S. refineries' waste treatment equipment of $255,000,000.

Fundamental Processes

A petroleum refinery is a complex combination of interdependent processes and operations, many of which are complex in themselves. In the development of the pollution profile for this industry twenty separate processes were determined to be fundamental operations essential to the production of the principal products from crude oil. They are presented, with brief definitions in a sequence as close to a refinery process flow sequence as such a complex combination permits.

Crude Oil and Product Storage - in tanks of varying size to provide adequate supplies of crude oils for primary fractionation runs of economical duration, to equalize process flows and provide feedstocks for intermediate processing units, and to store final products prior to shipment in adjustment to market demands. Water separates out during storage and is drawn off to the sewer.

Crude Desalting - electrostatic and chemical processes for removing inorganic salts and suspended solids from crude oil prior to fractionation. The crude oil is mixed with water to form an emulsion, which is broken by the action of an electrostatic field or specific demulsifying chemicals: the water sequesters the salts and other impurities from the crude oil, settles out, and is discharged to the sewer.

Crude Oil Fractionation - distillation to break heated crude oil into light overhead products, such as: gases and gasoline: kerosene, heating oil, gas oil, lube oil and other sidestream distillate cuts; and reduced crude bottoms. The trend is toward more complex combinations of atmospheric and vacuum towers with more individual sidestream products. The crude oil fractionation still or stills provide feedstocks for the downstream processing units and also some final products.

Thermal Cracking - includes visbreaking and coking as well as regular thermal cracking. In each of these operations heavy oil fractions are broken down into lighter fractions such as domestic heating oil, catalytic cracking stock, etc., by the action of heat and pressure: heavy fuels or coke are produced from the uncracked residue. Regular thermal cracking, which was an important process before the development of catalytic cracking is being phased out, but visbreaking and coking units are installed in a significant number of refineries, and their application is expected to increase.

Catalytic Cracking - like thermal cracking breaks heavy fractions, principally gas oils, into lighter fractions. This is probably the key process in production of large volumes of high-octane gasoline stocks; furnace oils and other useful middle distillates are also produced. The use of a catalyst permits operations at lower temperatures and pressures than with thermal cracking and inhibits the formation of undesirable polymerized products. Fluidized catalytic cracking processes, in which the finely-powdered catalyst is handled as a fluid, have very largely replaced the fixed-bed and moving bed processes, which use a beaded or pelleted catalyst.

Hydrocracking - basically catalytic cracking in the presence of hydrogen with lower temperatures and higher pressures than fluid catalytic cracking. The products are similar to catalytic cracking, but hydrocracking has greater flexibility in adjusting operations to meet changing product demands. It is one of the most rapidly growing refinery processes.

Reforming - a molecular rearrangement process to convert low-octane feedstocks to high-octane gasoline blending stock or to produce aromatics for petrochemical uses. Multi-reactor, fixed bed catalytic processes have almost completely replaced the older thermal process. There are many variations, but the essential and frequently the only difference is the composition of the catalyst involved.

Polymerization - a process to convert olefin feedstocks (primarily propylene) into a higher molecular weight polymer gasoline. This is a marginal process because the product octane is not sufficiently higher than that of the basic gasoline blending stocks to provide much help in up-grading the overall motor fuel pool, and because alkylation yields per unit of olefin feed are much better than polymerization yields. Consequently the current polymerization downtrend is expected to continue.

Alkylation - the reaction of an isoparaffin (usually isobutane) and an olefin (propylene, butylene, etc.) in the presence of a catalyst to produce a high octane alkylate, which is one of the most important components of automotive fuels. Sulfuric acid is the most widely used catalyst, although hydrofluoric acid and aluminum chloride are also used. Alkylation process capacity is expected to continue to increase with the demand for high-octane gasoline.

Isomerization - another molecular rearrangement process very similar to reforming. The charge stocks generally are lighter and more specific (normal butane, pentane and hexane). The desired products are isobutane for alkylation feedstocks and high octane isomers of the original feed materials for motor fuel.

Solvent Refining - includes a large number of alternative subprocesses designed to obtain high-grade lubricating oil stocks or aromatics, from feedstocks containing naphthenic, acidic, organo-metallic or other undesirable materials. Basically it is a solvent extraction process dependent on the differential solubilities of the desirable and undesirable components of the feedstock. The principal steps are countercurrent solvent extraction, separation of solvent and product by heating and fractionation, removal of traces of solvent from the product, and solvent recovery.

Dewaxing - removal of wax from lube oil stocks, generally after deasphalting and solvent refining, to produce lubricants with low pour points, and recover microcrystalline wax. Except for Pressing and Sweating, a strictly physical process now used very little, the various dewaxing processes use solvents, (principally methylethylketone, MEK) to promote wax crystallization.

Solvent is introduced into the waxy distillate stream at selected points in chilling equipment, and the wax is removed in vacuum filters. Through selection of feedstocks and variation of operating conditions the emphasis can be shifted from dewaxing of a lube oil stock to deoiling of a wax stock.

Hydrotreating - a process for the removal of sulfur compounds, odor, color and gum-forming materials, and other impurities from a wide variety of petroleum fractions by catalytic action in the presence of hydrogen. In most subprocesses the feedstock is mixed with hydrogen, heated and charged to the catalytic reactor. The reactor products are cooled, and the hydrogen, impurities, and high grade product separated. Hydrotreating was first used on lighter feedstocks, but with more operating experience and improved catalysts, it has been applied to increasingly heavy fractions such as lube oils and waxes. Along with hydrocracking, it is one of the most rapidly growing of refinery processes.

Deasphalting - removal of asphalt or resins from viscous hydrocarbon fractions, such as reduced crude, to produce stocks suitable for subsequent lube oil or catalytic cracking processes. This is a solvent extraction process, generally with propane as the solvent for the asphaltic materials. After contacting propane and the pipe still bottoms or other heavy stock in an extraction tower, the deasphalted oil overhead and asphaltic bottoms products are processed to remove and recover propane.

Drying and Sweetening - a relatively broad process category primarily to remove sulfur compounds, water and other impurities from gasoline, kerosene, jet fuels, domestic heating oils, and other middle distillate products. "Sweetening" pertains to the removal of hydrogen sulfide, mercaptans and elemental sulfur, which impart a foul odor and/or decrease the tetraethyl lead susceptibility of gasoline; the major sweetening operations are oxidation of mercaptans to disulfides, removal of mercaptans, and destruction and removal of all sulfur compounds (and elemental sulfur). Drying is accomplished by salt filters or adsorptive clay beds. Electric fields are sometimes used to facilitate separation of the product and the treating solution.

Wax Manufacture - the current widely used fractionation process for production of paraffin (and at times microcrystalline) waxes of low oil content is similar in most respects to MEK Dewaxing. The principal differences are the selection of a solvent or solvent mixture more suitable to the crystallization and separation of paraffin wax, and a more complicated crystallization-filtration flow involving redissolving and recrystallization.

Grease Manufacture - this process for the manufacture of various lubricating greases involves preparation of a soap base from an alkali earth hydroxide and a fatty acid, followed by addition of oil and special additives. The major equipment consists of an oil circulation heater, a high-dispersion contactor, a scraper kettle, and a grease polisher. Because of developments in sealed grease fittings and longer lasting greases, grease production is expected to continue to decline.

Lube Oil Finishing - Solvent refined and dewaxed lube oil stocks are further refined by clay or acid treatment to remove color-forming and other undesirable materials. Continuous Contact Filtration, in which an oil-clay slurry is heated and the oil removed by vacuum filtration, and Percolation Filtration, wherein the oil is filtered through clay beds, are the most widely used subprocesses. Percolation also involves naphtha washing and kiln-burning of spent clay to remove carbonaceous deposits and other impurities.

Blending and Packaging - Blending is the final step in producing finished petroleum products to meet quality specifications and market demands. The largest volume operation is the blending of various gasoline stocks (including alkylates and other high-octane components) and anti-knock (tetraethyl lead) anti-rust, anti-icing, and other additives. Diesel Fuels, lube oils, waxes, and asphalts are other refinery products which normally involve blending of various components and/or additives. Packaging at refineries is generally highly-automated and restricted to high-volume, consumer-oriented products such as motor oils.

Hydrogen Manufacture - the rapid growth of hydrotreating and hydrocracking has increased the newer refineries' demand for hydrogen beyond the level of byproduct hydrogen available from reforming and other refinery processes. Hydrogen is also in demand as a feedstock for ammonia and methanol manufacture. The most widely used subprocess is Steam Reforming, in which desulfurized refinery gases are converted to hydrogen, carbon monoxide, and carbon dioxide in a catalytic reaction; generally there is an additional shift converter to convert carbon monoxide to carbon dioxide.

The foregoing brief definitions are amplified in the discussion of Fundamental Processes in Appendix F.

Water Use and Reuse

Total water used in U. S. petroleum refineries, including recycle, increased 48.5 percent between 1954 and 1964 to an average daily usage of 16.8 billion gallons. During the same period the water intake increased by only 13.2 percent, which indicates a substantial increase in water reuse. Crude oil capacity increased 27 percent, and 1964 value added by manufacture was 70 percent higher than the corresponding 1954 figure.

The relationship between the increases in total water used and value added by manufacture is significant, because the change in value added reflects the increase in total products. and water usage is more closely related to total products than to crude capacity. The greater increase in value added (70 percent vs. 48.5 percent for water usage) shows that more product is being made with less water per product unit. Various surveys, as reported in the literature, support this trend toward lower water usage. A 1955 survey of 102 refineries showed an average wastewater effluent of 374 gallons per barrel of crude throughput, while a 1959 survey of 182 refineries showed an average of only 174 gallons. Interpretation of other data indicates wastewater discharge of 200, 100 and 50 gallons per barrel of crude for older, typical and newer refineries.

Cooling requirements are the major determinant of water usage. It is estimated that approximately 90 percent of the refineries' water requirements are for cooling. In the 1955 survey, one third of the refineries reused their cooling water 10-50 times, and only 17 refineries used once-through cooling systems. Refineries with recycle systems pumped about twice as much cooling water as the once-through refineries but withdrew only 4 percent as much water from the streams; actual water consumption (mostly evaporation losses) was, however, about 24 times greater for the recycle systems.

Some indication of the water requirements of specific processes is afforded by the much larger water usage of integrated refineries as compared to "topping" plants that use no cracking processes. The difference is attributed to the large volumes of cooling water required for thermal and catalytic cracking processes.

Another significant water usage is associated with the overhead condensers on vacuum fractionating towers. Most refineries use barometric condensers, which involve a direct water spray and consequently formation of oil emulsions that are hard to remove. With surface condensers, the cooling water does not come in contact with the hydrocarbons and therefore is available for reuse. Thus, replacement of barometric condensers by surface condensers should have two beneficial effects: increased water reuse, and reduction of wastewater volumes and loadings.

Several advances in cooling water technology indicate potential for water usage reductions. The use of air-cooled finned-tube exchangers in place of conventional cooling towers should sharply reduce water consumption because it would practically eliminate evaporation losses; it would also achieve additional benefits in connection with corrosion control and piping and pumping costs. Another potential area for reduction of cooling and heating requirements is in the reduction of intermediate storage by sophisticated computer control to maintain uniform product flow in a refinery. This would lessen the need to cool hot product from a primary processing unit and reheat it before changing to a downstream unit, and thus would reduce the overall cooling water requirement.

In summary, it can be seen that while the total quantity of petroleum products is increasing, the total water intake is leveling off. For the future, decreases in water usage and wastewater effluent quantities through more effective cooling practices are possible.

Manufacturing Process Utilization

A knowledge of the degree of application or use of the various fundamental and subprocesses is prerequisite to the development of any meaningful industry profile. Since an exhaustive compilation of every process in every refinery would be impractical, the analysis of process utilization in this report is confined to the major subprocess alternatives under each of the selected processes. In view of the availability of wastewater data (or more precisely the lack of such data) for many subprocesses, this restricted analysis will be just as useful a process basis for a pollution profile as would the elusive complete compilation. The use of the fundamental processes and major subprocesses in terms of percentage of total U. S. Refineries using each is presented in the main body of this report. The following tabulation summarizes the most significant points of the process pattern and in particular highlights the processing trends.

	Percentage of Refineries				
	1950	1963	1967	1972	1977
Thermal Cracking	59	48	45	40	35
Thermal Cracking-Regular		28	18	8	2
Coking		14	16	20	25
Visbreaking		13	16	18	22
Catalytic Cracking	25	51	56	60	65
Fluid Catalytic Cracking		39	45	50	60
Thermofor Catalytic Cracking		13	12	10	6
Houdriflow		3	4	2	0
Hydrocracking	0	2	8	25	34
Isomax			4	11	15
Unicracking			2	8	12
H-G Hydrocracking		0.3	0.8	3	3
H-Oil			0.4	1	1
Reforming		62	67	74	79
Platforming		37	40	44	47
Catalytic Reforming-Engelhard		5	9	11	12
Powerforming		1	2	3	3
Ultraforming		6	6	7	8

	Percentage of Refineries				
	1950	1963	1967	1972	1977
Polymerization	25	42	33	26	7
Alkylation	10	38	47	54	62
Sulfuric Acid		22	26	32	38
HF		16	21	22	25
Hydrotreating		47	56	70	80
Unifining		22	23	30	35
Hydrofining		3	3	5	8
Trickle Hydrodesulfurization		0.3	2	4	5
Ultrafining		3	5	8	10
Lube Oil Finishing		19	19	20	20
Percolation Filtration		11	7	5	2
Contin. Contact Filtration		6	7	7	7
Hydrotreating		2	5	8	11

In a number of cases the fundamental process figure and the sum of the listed subprocesses do not agree. There are two reasons for such apparent discrepancies. A single refinery may use two or more subprocesses in a given fundamental process area, such as Thermal Cracking; or all the applicable subprocesses may not be listed, e.g., Hydrotreating, where there are so many alternatives.

The degree of utilization can be expressed also in terms of capacities of the various processes and subprocesses as well as percentages of refineries using each. The difference between the two approaches is not significant in comparing subprocesses within a given fundamental process but is significant in establishing relationships between the fundamental processes. For example, in 1963 catalytic cracking was used in 51 percent of the nation's refineries, and polymerization in 42 percent, not a great difference; however, the combined capacity of the catalytic cracking units was more than 30 times that of the polymerization units.

One way of recognizing this factor in the subsequent development of wastewater volumes and loadings is the establishment of a series of categories to denote the general technology level of a refinery. In this series three levels of technology are defined:

Older - using relatively inefficient and/or obsolescent processes and subprocesses.

Typical - The processes and subprocesses most widely used today
Newer - using all or most of the advanced processes and subprocesses.

Thus, each subprocess is designated as older, typical or newer. This is not always clear cut, and in many cases a subprocess can be justifiably classified in more than one technology category. For example, the Platforming version of catalytic reforming is designated in all these categories because it has been used for many years, is the most widely used reforming process at present, and is still being installed in the newest and most modern refineries.

The 1950, 1963 and 1967 figures in the process utilization tabulation were based on the annual refinery surveys of The Oil and Gas Journal supplemented by other published data and results of specific refinery surveys. The projections for 1972 and 1977 involved several assumptions.

1. Decrease in number of refineries at rate of 2 percent per year.
2. Most of this decrease attributed to shutdown of smaller and less complex refineries.
3. Increase in crude capacity at a rate of 1.5 percent per year.
4. Increase in average capacity of newer subprocesses.
5. No change in average capacity of subprocesses being phased out.
6. No introduction of revolutionary new processes by 1977.

The assumptions concerning the number of refineries and subprocess unit capacities are based on analysis of industry practices and trends from 1935 to the present. The crude capacity increase is derived from industry forecasts of demand for petroleum products with consideration of the impact of imported crude and of the expectation of greater yields per barrel of crude. The prediction of no introduction of revolutionary new processes is based on the absence of any current new technological breakthrough and on the proposition that even if such a breakthrough were achieved in conceptual form this year, a resulting refinery process would require several years of development work before even limited use.

Projections of the subprocess mix were also influenced by projections of product demands and economic factors. For example, increasing demand for low sulfur fuels (based on air pollution considerations) will promote the use of hydrocracking and hydrotreating. At the same time, the relatively greater cost of hydrotreating will slow down the growth in situations where the newer drying-and-sweetening subprocesses can attain acceptable sulfur removals.

After delineation of the current and projected process utilization picture, the next step in development of the industry profile was to work up a combination of processes reflecting three levels of technology and three ranges of refinery size. Subprocesses most representative of older, typical, and newer technology were selected, and overall flow diagrams were prepared for refineries representatives of each stage of technology. There are some differences in the fundamental processes comprising these three hypothetical refineries because older methods are being phased out and newer ones are becoming increasingly important. This involves some divergence from the definition of fundamental processes as being essential to the manufacturing process, but in the ever changing petroleum industry what was essential in 1950 or 1963 is not necessarily still required in 1967, nor expected to be so in 1972 or 1977.

Refinery sizes ranges were established as: Small, under 35,000 bpsd; Medium, 35-100,000 bpsd; and Large, over 100,000 bpsd. The following table shows the percentage of U. S. Refineries in each of the size and technology categories.

	Refinery Size		
Technology	Small	Medium	Large
Older	31.2%	4.4%	0.4%
Typical	32.5%	17.4%	7.0%
Newer	3.4%	1.3%	2.4%
Total	67.1%	23.1%	9.8%

The use of these figures in assessing the contribution of each type of refinery to the total industry must be modified by consideration of crude capacity. This factor shows that the Large refineries (9.8 percent of the total) account for 45.7 percent of the total crude capacity, whereas the Small refineries (67.1 percent in terms of number of refineries) account for only 19.5 percent of the crude capacity.

Classification of existing refineries into the technology catagories presented some problems. There was sufficient information on processes and subprocesses to provide a substantial basis for classification in most instances, but numerous overlapping and single-purpose situations required the exercise of considerable judgment. The following examples illustrate the rationale of assignment. A relatively complete refinery that included both hydrocracking and isomerization was classified as "newer". A refinery with Thermofor catalytic cracking and polymerization but with neither alkylation nor hydrotreating was classified as "older". In many instances, particularly among the smaller refineries, the number of missing processes was so high that meaningful technological classification was not possible, and only 196 of the 261 refineries were classifed. The remaining refineries were divided between the older and typical technologies with a bias toward the older, because the hard-to-classify, very small refineries are also the least likely to keep pace with general technological advancement.

In view of the limitations imposed by the scarcity of wastewater data for specific subprocesses, the quantitative evaluation of waste loads is based on apportionment of total refinery effluent data to supplement the incomplete specific subprocess effluent data. Wastewater surveys from five refineries had pollutant concentration and wastewater flow data suitable for determination of subprocess waste loadings. These data and information on subprocess unit throughputs from other sources constituted the basis for quantitative waste load determination. It soon was apparent that the available data were not sufficiently comprehensive to support the original plan for development of wastewater quantities and pollutant loadings for small, medium, and large refineries in each technology level. For one thing, the data sources which were satisfactory on a subprocess basis did not include all refinery size ranges in each technology category. Thus, a hypothetical 100,000 bpsd refinery was selected as the base for quantitative waste evaluation for the three technology levels.

BOD, phenol and sulfide waste loadings were used in the quantitative evaluation, because experience has shown that these contaminants, along with wastewater flow, are the major determinants of wastewater treatment costs. Total refinery values for these three parameters and for wastewater flow were calculated by summation of the corresponding values for each fundamental refinery process. These data are summarized in the following tables along with similar data based on refinery effluents from API separators:

Summation of Individual Processes

Technology	Flow mgd	BOD lbs/day	Phenol lbs/day	Sulfide lbs/day
Older	23.1	12,500	3,500	2,200
Typical	9.9	5,400	1,650	625
Newer	4.5	4,200	850	680

After API Separator

Technology	Flow mgd	BOD lbs/day	Phenol lbs/day	Sulfide lbs/day
Older	25.0	40,000	3,000	1,000
Typical	10.0	10,000	1,000	300
Newer	5.0	5,000	500	300

The wastewater flow based on total effluent after API Separators is somewhat higher, probably because flow data were not available for some processes and because of significant variations in cooling water practices. The BOD waste load in each technology category is higher for total effluent than for the summation. There are two reasons for this difference: lack of BOD data for a few processes and, more significantly, the contribution of leaks, spills and other non-process sources. The much small discrepancy in the newer refineries indicates the non-process sources as the principal explanation. On the other hand, phenol and sulfide loadings are consistently lower on the total refinery effluent basis. Phenol is partially extracted by oil and is removed along with oil in the API separators. Sulfide concentrations in the refinery sewers are reduced by turbulence, temperature and lower pH and by removal in sour water strippers at various processing units.

Waste loads were also calculated on the basis of units of major refinery products. This involved allocation of the overall refinery and specific process waste loadings to specific products based on average national yields of these products and the connection between specific processes and specific products.

Total industry waste loads and wastewater flow were projected to 1977. Waste loads were projected on the basis of an annual rate of increase of 3.6 percent, based on a compromise of industry forecasts and projections of crude throughput and product value added. The wastewater flow projection was more moderate, an approximate increase of 1 percent per year, because of strong trends in the industry in improvement of cooling water practices.

Refinery throughput and the output of major products were reviewed for evidences of seasonal waste production patterns but no appreciable variations were detected, despite seasonal changes in demands for gasoline and domestic heating oil.

Waste Reduction Practices

Evaluation of the effectiveness of in-plant processing changes in reducing wastewater pollution was qualitative and general, rather than quantitative and specific. In regard to the relative pollution effects of specific processes, the most significant developments have been hydrocracking and hydrotreating. Each of these processes generates substantially lower pollution loadings than the processes they are replacing; available data on pollutant concentrations in the unit wastewater streams indicates that these processes have significantly reduced sulfide and spent caustic waste loadings. A more general indication of pollution reduction by in-plant processing practices is the much lower pollutant loadings per unit of throughput for "newer" refineries as compared to "older" or "typical" refineries. This reduction is attributed in large measure to decreased losses to the sewers by sampling and water drawoff operations in the "newer" refineries, where facilities, controls, and general operating practices are likely to be superior.

Waste treatment methods applicable to petroleum refineries can be divided into five types: Physical, Chemical, Biological, Tertiary, and Special In-Plant methods.

Physical methods include gravity separators, air flotation (without chemicals), and evaporation. Gravity separators (API and earthen basins), which are used in practically all refineries, are designed primarily for removal of floatable oil and settleable solids. They remove 50-99% of the separable oil and 10-85% of the suspended solids: concurrently with these principal functions they remove BOD, COD, and phenol, at times to a substantial degree depending on the influent wastewater characteristics. Air flotation without chemical addition obtains comparable results. Pollutant removals by evaporation ponds are very high, but the application of this method is severely limited by location, climate, and land availability considerations.

Chemical methods (Coagulation-sedimentation and chemically assisted air flotation) are more effective in oil and solids removal, particularly in respect to emulsified oil.

The biological methods include activated sludge, trickling filters, aerated lagoon, and oxidation ponds. In general these treatment processes require wastewater pretreatment to remove oil and remove or control other conditions (such as pH and toxic substances). The Activated Sludge process is the most effective for removal of organic materials (which is the main purpose of biological treatment): expected removal efficiencies are 70-95% for BOD, 30-70% for COD, and 65-99% for phenols and cyanides.

Tertiary treatment to date has been limited to activated carbon and ozonation, which are effective in removing taste and odor elements and refractory organic substances from biologically treated wastewaters.

The most important in-plant treatment methods are sour water stripping, neutralization and oxidation of spent caustics, ballast water treatment, slop oil recovery, and temperature control. These measures substantially reduce the waste loadings in the influent to general refinery treatment facilities, and to a significant degree are necessary to insure reasonable performance of the general treatment facilities.

The extent of use of various waste treatment practices was reviewed. Practically all of today's refineries use gravity separators, but only 5-10% have chemical treatment facilities. Approximately one-fourth have oxidation ponds, but substantially fewer (5-7%) use the more effective biological treatment processes. Projection of the extent of use to 1977 indicates: continued full application of gravity separators, with API separators replacing most of the earthen basin types; chemical treatment processes in 15-20% of the refineries; greatly increased use of biological treatment processes, with essentially all refineries using biological treatment, including 55% using the Activated Sludge process; approximately 5% utilization of tertiary treatment. The projections reflect the assumption of more comprehensive and more stringent water and air pollution regulations.

In considering the effectiveness of individual waste treatment processes, it is essential that they be arranged in proper sequence and that segregation of "clean" wastewaters and other pretreatment measures be properly evaluated.

Discharge of refinery wastewater to municipal sewers has not been a significant factor in refinery pollution control, primarily because of prohibition of discharges of oil and inflammable and

and explosive materials. However, with proper pretreatment, including oil, sulfide and phenol removal, disposal via municipal systems is technically feasible and could be economically advantageous.

Byproduct utilization, defined as disposal of materials to accrue some economic benefit but not enough to cover the cost of recovery, is limited. The only really significant byproduct apparent at the present time is sulfur, which is recovered from sour water and hydrotreating processes. The value of the sulfur so recovered in 1966 has been estimated at $40,000,000.

Waste Treatment Costs

A comprehensive report on waste treatment costs in the petroleum refining industry in 1959 indicated that on the basis of 183 refineries reporting (out of a possible 313) replacement and operating costs for waste treatment processes totalled $156,000,000 and $30,000,000 respectively. These costs were calculated by extrapolating to account for 100 percent of the crude capacity at that time. In 1959, planned additions to waste treatment facilities for 134 refineries totalled $29,000,000.

The data from this 1959 report were used as the basis for calculation of replacement value and operating costs for 1966. The factors used to update the data were assumption of a 30 percent increase in construction and operating costs, and extrapolation of the value of the 1959 planned additions for 134 refineries to cover the 1966 total of 279 refineries. In this manner the 1966 wastewater facilities replacement value was estimated to be $275,000,000 and the related annual operating costs $55,000,000.

Capital and annual costs for 10-12 specific waste treatment processes required for adequate overall refinery, or end-of-pipe, treatment were calculated for small, medium, and large refineries in the older, typical, and newer technology categories. For purposes of this calculation, the following throughput were used: small - 30,000 bpsd; medium - 75,000 bpsd; large - 150,000 bpsd. The capital costs were based on estimates of 1967 construction costs (including a 15% contingency allowance) but did not include design or other engineering fees. The annual costs, also 1967 estimates, included operating labor, maintenance, utilities, and chemicals costs but no fixed charges for depreciation, interest, taxes, etc.

These end-of-pipe treatment costs were then prorated among the various fundamental refinery processes on the basis of wastewater flow and BOD loading of each fundamental process. Ideally the final step in this cost allocation procedure would have been to spread the cost of each waste treatment process over each of the fundamental processes for small, medium, and large refineries in each of the three technology levels. However, this would have required more than 100 separate tables, and to overcome this formidable obstacle and at the same time obtain a reasonable estimate of treatment cost allocation, three end-of-pipe wastewater treatment trains were developed to represent low, intermediate, and high degrees of treatment. These were defined as follows:

Low - API Separator and Slop Oil Treatment
Intermediate - Low, plus Aerated Lagoon and Sour Water Stripping
High - Low, plus Activated Sludge, Sour Water Stripping, Sludge Thickening and Vacuum Filtration, and Sludge Incineration.

The cost allocations for a typical refinery are presented in the following table.

	Percent of Total Treatment Cost					
	Low Degree		Inter. Degree		High Degree	
Fundamental Process	Capital	Annual	Capital	Annual	Capital	Annual
Crude Oil Storage	1.9	2.7	1.6	2.5	2.4	2.7
Crude Oil Desalting	7.0	4.6	3.4	2.8	2.5	2.3
Crude Oil Fractionation	50.1	50.0	41.2	45.0	34.2	35.4
Thermal Cracking	5.3	3.5	6.2	3.8	2.6	1.6
Catalytic Cracking	17.6	16.6	19.7	17.8	14.4	13.5
Hydrocracking	2.6	1.7	4.5	2.8	1.9	1.0
Reforming	0.6	0.8	0.5	0.8	0.6	0.6
Polymerization	0.7	0.9	0.6	0.9	0.7	0.9
Alkylation	1.7	2.4	1.5	2.3	1.8	2.2
Solvent Refining	0.4	0.4	0.2	0.3	0.3	0.3
Dewaxing	0.4	0.6	0.4	0.6	5.5	5.7
Hydrotreating	0.2	0.3	5.4	3.3	2.5	1.6
Drying-and-Sweetening	9.6	13.3	11.4	14.9	17.9	19.6
Other	1.9	2.2	3.2	2.2	12.7	12.6

Examination of this table discloses that Crude Oil Fractionation, Catalytic Cracking, and Drying-and-Sweetening account for the major shore of the treatment costs, with Drying-and-Sweetening becoming more prominent as the degree of waste treatment advances.

Although detailed cost information for justification of in-plant processing measures for pollution abatement is not available, an indication of their economic value is afforded by analysis of the effects of reduction of organic and hydraulic loadings on treatment costs. Data for a 100,000 bpsd refinery, with a "high" degree of waste treatment as previously defined, indicate that a 50% reduction in BOD loading (with wastewater flow unchanged) would effect a 15% reduction in capital cost of the treatment facilities. A 50% reduction in wastewater flow (with BOD loading unchanged) would effect a 20% reduction. If both BOD and flow are reduced 50%, the capital cost would be reduced by 32%.

FUNDAMENTAL PROCESSES

Introduction

A petroleum refinery is a complex combination of interdependent operations and processes, which can be divided into six major groups:

1) Storage - e.g., of crude oil, intermediates, and final products
2) Fractionation - e.g., distillative separation and vacuum fractionation
3) Decomposition - e.g., thermal cracking, catalytic cracking, and hydrocracking
4) Hydrocarbon Rebuilding and Rearrangement - e.g., polymerization, alkylation, reforming, isomerization
5) Extraction - e.g., solvent refining, solvent dewaxing
6) Product Finishing - e.g., drying-and-sweetening, lube oil finishing, blending and packaging.

For this pollution profile, twenty separate processes have been selected as the fundamental processes essential to production of final products from crude oil. They are presented, with brief definitions, in a sequence as close to a refinery process flow sequence as such a complex combination permits.

The major sources for the process descriptions were the "1966 Refining Process Handbook" of Hydrocarbon Processing magazine (1) and W. L. Nelson's Petroleum Refinery Engineering (2). Information regarding the wastes from each process was obtained from ROY F. WESTON files (3), personal interviews (4), and Aqueous Wastes from Petroleum and Petrochemical Plants by W. R. Beychok (5).

Crude Oil and Product Storage - in tanks of varying size to provide adequate supplies of crude oils for primary fractionation runs of economical duration, to equalize process flows and provide feedstocks for intermediate processing units, and to store final products prior to shipment in adjustment to market demands. Water separates out during storage and is drawn off to the sewer.

Crude Desalting - electrostatic and chemical processes for removing inorganic salts and suspended solids from crude oil prior to fractionation. The crude oil is mixed with water to form an emulsion, which is broken by the action of an electrostatic field or specific demulsifying chemicals; the water sequesters the salts and other impurities from the crude oil, settles out, and is discharged to the sewer.

Crude Oil Fractionation - distillation to break heated crude oil into light overhead products, such as: gases and gasoline; kerosene, heating oil, gas oil, lube oil and other sidestream distillate cuts; and reduced crude bottoms. The trend is toward more complex combinations of atmospheric and vacuum towers with more individual sidestream products. The crude oil fractionation still or stills provide feedstocks for the downstream processing units and also some final products.

Thermal Cracking - includes visbreaking and coking as well as regular thermal cracking. In each of these operations heavy oil fractions are broken down into lighter fractions such as domestic heating oil, catalytic cracking stock, etc., by the action of heat and pressure; heavy fuels or coke are produced from the uncracked residue. Regular thermal cracking, which was an important process before the development of catalytic cracking is being phased out, but visbreaking and coking units are installed in a significant number of refineries, and their application is expected to increase.

Catalytic Cracking - like thermal cracking breaks heavy fractions, principally gas oils, into lighter fractions. This is probably the key process in production of large volumes of high-octane gasoline stocks; furnace oils and other useful middle distillates are also produced. The use of a catalyst permits operations at lower temperatures and pressures than with thermal cracking and inhibits the formation of undesirable polymerized products. Fluidized catalytic cracking processes, in which the finely-powdered catalyst is handled as a fluid, have very largely replaced the fixed-bed and moving bed processes, which use a beaded or pelleted catalyst.

Hydrocracking - basically catalytic cracking in the presence of hydrogen with lower temperatures and higher pressures than fluid catalytic cracking. The products are similar to catalytic cracking, but hydrocracking has greater flexibility in adjusting operations to meet changing product demands. It is one of the most rapidly growing refinery processes.

Reforming - a molecular rearrangement process to convert low-octane feedstocks to high-octane gasoline blending stock or to produce aromatics for petrochemical uses.

Multi-reactor, fixed bed catalytic processes have almost completely replaced the older thermal process. There are many variations, but the essential and frequently the only difference is the composition of the catalyst involved.

Polymerization - a process to convert olefin feedstocks (primarily propylene) into a higher molecular weight polymer gasoline. This is a marginal process because the product octane is not sufficiently higher than that of the basic gasoline blending stocks to provide much help in up-grading the overall motor fuel pool, and because alkylation yields per unit of olefin feed are much better than polymerization yields. Consequently the current polymerization downtrend is expected to continue.

Alkylation - the reaction of an isoparaffin (usually isobutane) and an olefin (propylene, butylene, etc.) in the presence of a catalyst to produce a high octane alkylate, which is one of the most important components of automotive fuels. Sulfuric acid is the most widely used catalyst, although hydrofluoric acid and aluminum chloride are also used. Alkylation process capacity is expected to continue to increase with the demand for high-octane gasoline.

Isomerization - another molecular rearrangement process very similar to reforming. The charge stocks generally are lighter and more specific (normal butane, pentane and hexane). The desired products are isobutane for alkylation feedstocks and high-octane isomers of the original feed materials for motor fuel.

Solvent Refining - includes a large number of alternative subprocesses designed to obtain high-grade lubricating oil stocks or aromatics, from feedstocks containing naphthenic, acidic, organo-metallic or other undesirable materials. Basically it is a solvent extraction process dependent on the differential solubilities of the desirable and undesirable components of the feedstock. The principal steps are countercurrent solvent extraction, separation of solvent and product by heating and fractionation, removal of traces of solvent from the product, and solvent recovery.

Dewaxing - removal of wax from lube oil stocks, generally after deasphalting and solvent refining, to produce lubricants with low pour points, and recover microcrystalline wax. Except for Pressing and Sweating, a strictly physical process now used very little, the various dewaxing processes use solvents, (principally methylethylketone, MEK) to promote wax crystallization.

Solvent is introduced into the waxy distillate stream at selected points in chilling equipment, and the wax is removed in vacuum filters. Through selection of feedstocks and variation of operating conditions the emphasis can be shifted from dewaxing of a lube oil stock to deoiling of a wax stock.

Hydrotreating - a process for the removal of sulfur compounds, odor, color and gum-forming materials, and other impurities from a wide variety of petroleum fractions by catalytic action in the presence of hydrogen. In most subprocesses the feedstock is mixed with hydrogen, heated and charged to the catalytic reactor. The reactor products are cooled, and the hydrogen, impurities, and high grade product separated. Hydrotreating was first used on lighter feedstocks, but with more operating experience and improved catalysts, it has been applied to increasingly heavy fractions such as lube oils and waxes. Along with hydrocracking, it is one of the most rapidly growing of refinery processes.

Deasphalting - removal of asphalt or resins from viscous hydrocarbon fractions, such as reduced crude, to produce stocks suitable for subsequent lube oil or catalytic cracking processes. This is a solvent extraction process, generally with propane as the solvent for the asphaltic materials. After contacting propane and the pipe still bottoms or other heavy stock in an extraction tower, the deasphalted oil overhead and asphaltic bottoms products are processed to remove and recover propane.

Drying and Sweetening - a relatively broad process category primarily to remove sulfur compounds, water and other impurities from gasoline, kerosene, jet fuels, domestic heating oils, and other middle distillate products. "Sweetening" pertains to the removal of hydrogen sulfide, mercaptans and elemental sulfur, which impart a foul odor and/or decrease the tetraethyl lead susceptibility of gasoline; the major sweetening operations are oxidation of mercaptans to disulfides, removal of mercaptans, and destruction and removal of all sulfur compounds (and elemental sulfur). Drying is accomplished by salt filters or adsorptive clay beds. Electric fields are sometimes used to facilitate separation of the product and the treating solution.

Wax Manufacture - the current widely used fractionation process for production of paraffin (and at times microcrystalline) waxes of low oil content is similar in most respects to MEK Dewaxing. The principal differences are the selection of a solvent or solvent mixture more suitable to the crystallization and separation of paraffin wax, and a more complicated crystallization-filtration flow involving redissolving and recrystallization.

Grease Manufacture - this process for the manufacture of various lubricating greases involves preparation of a soap base from an alkali earth hydroxide and a fatty acid, followed by addition of oil and special additives. The major equipment consists of an oil circulation heater, a high-dispersion contactor, a scraper kettle, and a grease polisher. Because of developments in sealed grease fittings and longer lasting greases, grease production is expected to continue to decline.

Lube Oil Finishing - Solvent refined and dewaxed lube oil stocks are further refined by clay or acid treatment to remove color-reforming and other undesirable materials. Continuous Contact Filtration, in which an oil-clay slurry is heated and the oil removed by vacuum filtration, and Percolation Filtration, wherein the oil is filtered through clay beds, are the most widely used subprocesses. Percolation also involves naphtha washing and kiln-burning of spent clay to remove carbonaceous deposits and other impurities.

Blending and Packaging - Blending is the final step in producing finished petroleum products to meet quality specifications and market demands. The largest volume operation is the blending of various gasoline stocks (including alkylates and other high-octane components) and anti-knock (tetraethyl lead) anti-rust, anti-icing, and other additives. Diesel Fuels, lube oils, waxes, and asphalts are other refinery products which normally involve blending of various components and/or additives. Packaging at refineries is generally highly-automated and restricted to high-volume, consumer-oriented products such as motor oils.

Hydrogen Manufacture - the rapid growth of hydrotreating and hydrocracking has increased the newer refineries' demand for hydrogen beyond the level of byproduct hydrogen available from reforming and other refinery processes. Hydrogen is also in demand as a feedstock for ammonia and methanol manufacture. The most widely used subprocess is Steam Reforming, in which desulfurized refinery gases are converted to hydrogen, carbon monoxide, and carbon dioxide in a catalytic reaction; generally there is an additional shift converter to convert carbon monoxide to carbon dioxide.

The foregoing brief definitions are amplified in the discussion of Fundamental Processes in Appendix F.

Simplified process flow diagrams for representative subprocesses in most of the fundamental process areas are presented in Figures 5 through 24.

WATER USE AND REUSE

General

Total water used in the U. S. petroleum refineries, including recycle, increased from 11.3 billion gallons per day (bgd) in 1954 to 16.8 bgd in 1964, an increase of 48.5%. Water intake during this period increased only 13.2%, indicating a substantial rise in water reuse. In 1954 70% of the total water used was provided by recycle, while in 1964 77% was provided by recycle (8). The reuse ratio (total water used divided by water intake) increased from 3.3 to 4.4 during this period.

Future implications of water use can be best understood by relating water use to refinery operation. The crude oil capacity increased 27% during the 1954-64 period while the value added by manufacture increased 70%. The following table summarizes these increases.

	Percent Increase 1954-64
Total Water Used	48.5%
Total Water Intake	13.2%
Crude Oil Capacity	27%
Value Added by Manufacture	70%

The most meaningful data in this table are the total water used and the value added by manufacture, because value added reflects the increase in total products generated and total water usage is more closely related to total products than to crude capacity. The main point in this discussion of water use and reuse is that more products are being produced with less water. To further support this conslusion, unit water discharged expressed as gallons of water used per barrel of crude processed is a meaningful yardstick. A 1955 survey (9) of 102 refineries indicated an average effluent of 374 gallons per barrel of crude, and a 1959 survey (10) of 182 refineries indicated an average of 170 gallons per barrel. Approximately 25 individual refinery effluents covering various size refineries with varying degrees of technology were also reviewed. An interpretation of all the data available indicates an older refinery discharges 200 gallons of wastewater per barrel of crude; a typical refinery, 100 gallons per barrel; and a new refinery, 50 gallons per barrel. As larger, more integrated refineries are built, wastewater effluent unit volume will decrease.

The following tabulation summarizes the various uses of the water withdrawn from surface and ground water sources by petroleum refineries.

Use of Water Withdrawn by U.S. Petroleum Refineries-1964

	Billion Gallons per year	Percent of Intake
Cooling and Condensing	1,125	81.0
Steam for Power Generation	81	5.8
Boiler Feedwater and Sanitary Service	98	7.1
Process	84	6.1
Total Intake	1,388	100.0
Total Water Used (including recirculation and reuse)	6,146	

Very little, if any process water is reused. One eastern refinery uses spent caustic from neutralization of alkylation process wastes as make-up to the barometric condensers on the vacuum distillation stills. However, severe emulsion problems have arisen and the procedure is being abandoned. Some refineries have used sulfidic wastes from separation operations in the cracking processes to control temperature in a fluid catalytic cracker by injecting the wastes into the reaction zone. Again problems have been created by the recycle of metals and tars, which tend to gum or poison the catalysts.

The API Manual on Disposal of Refinery Wastes (Vol. III, p. 33) lists many situations where process waters can be reused, such as reuse of phenolic wastewaters or sulfide stripped condensate as make-up water to a crude oil desalter. Only a small number of refineries employ any of these methods, and even then only on a limited basis.

Only 6.1% of water withdrawn is used for process water and based on gross water used, process waters constitute only 1.4% of total water used. Information on process water reuse in the industry is not available, but reuse is probably insignificant. The most fruitful area of water reuse is cooling water recirculation.

Water Requirements

In 1955 91% of the water requirements of the petroleum refineries surveyed was for cooling. One third of the refineries reused their cooling water from 10 to more than 50 times, and only 17 refineries used once-through cooling systems. Refineries with recirculating cooling systems circulated about twice as much water as refineries using once-through cooling systems, but needed only 4 percent as much raw water supply. Evaporation loss (actual water consumed) was about 24 times greater for the recirculating system.

Refineries which did not have cracking operations used considerably less water than the more integrated plants having cracking operations, primarily because of the large volumes of water required for thermal and catalytic cracking processes.

Vacuum fractionation of crudes and reduced crudes is used in essentially all refineries, and the steam jet ejector is the most widely used method of producing a vacuum for these fractionation processes. Ejectors use steam which is expanded through a nozzle to create the vacuum. The steam vapors and the vapors removed from the fractionator must be condensed. For certain processes having rich overhead vapors a product cooler, such as a shell-and-tube heat exchanger, is used to condense and recover the valuable organics. The remaining condensables must be removed prior to discharge of the vapor stream to the atmosphere, and the most commonly used method is a direct water spray in a chamber called a barometric condenser. The organics, oils, and steam condensate are intimately mixed in a large volume of colling water. This mixing and dilution tends to form oil emulsions which are very difficult to remove.

In some refineries surface condensers are used instead of barometric condensers. These usually consist of a series of shell-and-tube heat exchangers in which the condensable materials are removed and the water used for cooling does not come in contact with the condensate. In many cases the condensate is highly concentrated and can be recovered, incinerated, or treated separately. The cooling water is not contaminated by the oils and organics, and can be reused again after removal of the heat. While surface condensers are far superior to the barometric condensers, they are most costly to install, have higher maintenance and operation costs, and have a shorter equipment life. Surface-condensing steam jets are being installed in the newer refineries and will play an important role in reduction of wastewater effluents.

There are several advances in technology that will reduce cooling requirements and subsequently cooling water usage. In arid regions where water is at a premium, the use of finned-tube coolers is becoming important. This cooling method employs forced air flow over a bank of finned tubes through which the spent cooling water is passed. Heat is transferred from the water through the tubes to the air stream by convection and radiation. The greatest single advantage of this process is that the water is contained in a completely closed system and requires minimal make-up water. Another advantage is that very high quality water can be used and corrosion can be virtually eliminated. Other indirect benefits of reduction in total water usage are smaller pipelines for water transport and lower water pumping costs.

Maintaining uniform product flow in a refinery is a desirable goal, but involves rigid control and is quite difficult. The normal procedure today where in-process inventory is required is to take a hot product from a given process, cool it and store it to provide an inventory of intermediate products for further processing. Before the intermediate product can be further processed, it must be reheated. If the use of computers and other technological advances can reduce the amount of intermediate storage and consequently the amount of heating and cooling required, the total cooling water requirements of the refinery could be reduced.

Thus it can be seen that while the total quantity of petroleum products is increasing the amount of water intake is leveling off. In the future, decreases in wastewater effluent quantities through more effective cooling practices are possible.

MANUFACTURING PROCESS UTILIZATION

General Approach

To develop an understanding of the overall pollution profile for the petroleum industry, it is imperative that the parts contributing to the whole be understood. The ideal solution would involve detailed data on the subprocess mix of the industry, output for each subprocess, and wastewater quantities and characteristics for each subprocess per unit of output. Even if a completely accurate profile of the present conditions could be developed, there would still be a number of important questions to be answered. What was the profile in the past? What will it be in the future? What are the factors contributing to the changes? How is the pollution picture affected by refinery size, degree of technology, sources and characteristics of raw materials, refinery location, combinations of refinery processes, and sequence or combination of waste treatment processes? Can total impact of pollution be measured solely by costs?

An understanding of all these factors for an industry with such complex processing as petroleum refining would involve a study so comprehensive that the time required would preclude its usefulness as a projection of future conditions and as a guide for appropriate action. Lack of precise information, particularly in regard to wastes from specific subprocesses, is one of the major complications. Nevertheless, some basis must be chosen that will reflect the best attainable understanding of the pollution picture for the present and for the specified future period. The principal bases for the selected approach are: estimates of waste quantities and characteristics from the most significant subprocesses; size of refinery; and general level of technology.

Current and Future Subprocess Utilization

For this approach it is necessary to know which subprocesses are being used in the industry and which subprocesses are expected to be used in the future. Table 1 summarizes the fundamental process and subprocess utilization percentages in the U. S. petroleum industry for 1963 and 1967, as well as the expected percentages for 1972 and 1977. It also includes limited information about fundamental processes and subprocesses for 1950. The industry process use is expressed in terms of percent of refineries using each process or subprocess, with the principal subprocesses in each fundamental process area listed. There are some discrepancies between the fundamental process total and the sum of the listed subprocesses, either because all applicable subprocesses are not listed or because a single refinery may use two or more subprocesses in a given fundamental process area. This latter situation is frequently the result of modernization-expansion where economic and technological considerations indicate the addition of a new type of processing unit but not the retirement of an existing facility.

It must be pointed out again that the percentages given in Table 1 are based on the number of refineries using the subprocesses and not on the basis of feed capacity. This difference is not very significant when comparing subprocesses under a fundamental process, but it can be significant when comparing fundamental processes. For example, in 1963 catalytic cracking was utilized in 51 percent of the nation's refineries and polymerization was employed in 42 percent. These figures are fairly close, but the total industry feed capacities of the two processes were very different; the feed capacity of catalytic cracking was more than 30 times that of polymerization.

The "O", "T", and "N" notations under the "Technology" heading in Table 1 refer to whether the subprocess would usually be found in an "older", "typical", or "newer" refinery. An "older" refinery is one that uses a relatively inefficient subprocess series. "Typical" refers to a refinery that employs the subprocesses most widely used today. A refinery classed as "newer" is one that makes use of all or most of the more advanced subprocesses. Some subprocesses, such as Platforming, are rated as being older, typical, and newer; these have been used for many years, are prominent today, and still are being included in the newest refineries. Identification of a subprocess as being older, typical, or newer was done on the basis of interviews with industry representatives (4) and a survey of the literature.

Most of the figures given in Table 1 for the years 1950, 1963, and 1967 are from the annual survey of United States refineries by The Oil and Gas Journal (11, 12, 13, 14, 15). As is the case throughout this report, data were available on the major refining processes such as the cracking processes, reforming, polymerization, alkylation, isomerization, and hydrotreating. Information on the number of plants using the other fundamental processes and their subprocesses was not nearly as complete, and some estimates had to be made; these estimates were based on incomplete surveys of operating refineries and total production figures (1, 16, 17, 18, 19, 20, 21). The close inter-relationship of many fundamental processes was used here as in many other sections of this profile to aid in making the most accurate estimate possible.

For example, the feed into wax finishing processes comes almost entirely from dewaxing operations. The estimate of the percent of plants using wax finishing was thus the same as indicated by published data for percent of refineries using dewaxing.

Projected Subprocess Mix

The expected subprocess mix for 1972 and 1977 was obtained by projecting the data from 1963 and 1967 and using the following assumptions:

1. The number of refineries will decrease at a rate of 2 percent per year between 1967 and 1977.
2. Most of the decrease in the number of refineries will be due to the shutdown of small refineries using only a few fundamental processes.
3. Crude capacity will increase at the rate of 1.5 percent per year between 1967 and 1977.
4. The average unit capacities of subprocesses coming into greater use will increase.
5. The average unit capacities of subprocesses going out of use will remain the same.
6. No revolutionary processes will be introduced and widely adopted between 1967 and 1977.

The first assumption is based on published data showing a continuing drop in the number of U. S. refineries since 1935 (11, 13, 14). The second, fourth, and fifth assumptions are discussed or indicated by data given in the same sources. The increase of crude capacity of 1.5 percent per year was based on past increases of crude capacity (1.2 percent per year from 1960 to 1967) and forecasts of a 3 percent per year increase in petroleum product demand between now and 1980 (22, 23). The produce demand figure is reduced by the increasing percentage of imports (23) and the larger volume of petroleum products obtained from each barrel of crude oil processed. The last assumption is based on the fact that no revolutionary process is presently foreseen and even if one were discovered tomorrow, it would take several years of testing before it would come into even limited use.

Projections of product demand were also used to project the subprocess mix. For example, increasing demand for low-sulfur fuels from air pollution considerations will result in increased use of hydrocracking and hydrotreating, because these processes produce fuels with a low-sulfur content. The demand for grease is expected to remain fairly constant or decrease slightly: thus grease manufacturing remains unchanged as to the percent of plants using it.

Projections of the 1963 and 1967 data were also modified by other economic considerations. Drying-and-sweetening of petroleum products is used mainly to desulfurize the product. It is being replaced by hydrotreating because hydrotreating removes a higher percentage of the sulfur. However, hydrotreating is more expensive, and drying-and-sweetening will remain in use for treating some products; the volume of products treated will be greatly reduced, but the percentage of plants using drying-and-sweetening will remain about the same.

Trends in subprocess changes indicated in the literature and summarized in the fundamental process descriptions also influenced the projections, as did process inter-relationships. An increase in alkylation creates a demand for isobutane feed, which could mean more need for isomerization. But hydrocracking is also a source of isobutane, and since hydrocracking is increasing in use because of its flexibility, it can also be used to provide isobutane and thus limit the increase in isomerization. The growth of hydrogen manufacture is also linked to hydrocracking in that reforming cannot meet the hydrogen demands of isomerization, hydrotreating, and hydrocracking.

Technology Level and Refinery Size

After delineation of the subprocesses, the next step in preparation of the industry profile was development of a combination of processes reflecting three levels of technology and three ranges of refinery size. From each fundamental process listed in Table 1 subprocesses most representative of older, typical, and newer processing technology were selected. These subprocesses formed the bases for three flow diagrams (See Figures 1, 2, and 3) which present three hypothetical refineries - one for each stage of technology. These flow diagrams were developed from consulting and direct experience in the petroleum industry, from literature review, and from special interviews with refinery technical personnel.

There are some differences in the fundamental processes comprising each of these hypothetical refineries, because some older fundamental processes are being phased out and some newer ones are becoming increasingly important. This involves some divergence from the original contract definition of fundamental processes as being essential to the manufacturing process, but in the ever-changing petroleum industry, what was essential in 1950 or 1963 is not necessarily essential in 1967 nor expected to be so in 1972 or 1977. Because of the complexity of the industry and variations in growth patterns, there are few, if any, refineries in the United States that have the exact combination of subprocesses presented in the three flow diagrams. A recent survey in The Oil and Gas Journal (11) illustrates the difficulty in determination of a representative refinery. In this survey of 261 operating refineries in the U. S. in 1967, information was obtained concerning capacity and extent of use of the following processes: vacuum distillation, thermal operations (thermal cracking, coking, visbreaking), catalytic cracking, reforming, hydrotreating, alkylation, polymerization, lube oil production, cake production, and asphalt production. Only two of the refineries surveyed had all of the processes listed; 14 lacked one of the processes, 23 lacked two, 30 lacked three, and 194 lacked four or more of the processes. Despite the lack of any significant number of existing refineries with exactly comparable facilities, the classification and diagramming of these three hypothetical refineries is a useful step in development of a reliable overall estimate of industry conditions and trends.

It should be pointed out that the process sequence shown in Figures 1, 2, and 3 have been simplified to the extent that not all of the possible process streams are shown. The process streams included in the flow diagrams were restricted to those necessary to show how an integrated refinery produces its major products; the actual situation is much more complex. For example, most refineries produce two or more grades of finished gasoline, and these may be blended from six or more separate blending stocks; yet, for purposes of clarity and simplicity the process flow diagrams have only one gasoline stream.

The capacities shown for the various processes are the total refinery capacities of those processes. In practice these may be the sum of several process unit capacities at different locations in the refinery rather than the capacity of a single unit. For example, although hydrotreating is shown only at one location in the "typical" refinery, there may be several hydrotreating units at different locations. The process locations shown, however, do represent the manner in which the most significant part of the capacity of a given process is arranged.

The next factor to be considered was refinery size. Table 2 gives a breakdown of the number of refineries by size and technology. A "small" refinery has been defined as one with a crude capacity of 35,000 bpsd or less, "medium" a capacity of 35,000 to 100,000 bpsd, and "large" a capacity greater than 100,000 bpsd. The percentage of refineries in each size range and the crude capacity ranges were taken from the literature (24). It is important to note that the "large" refineries constitute only 9.8 percent by number but 45.7 percent of the total crude capacity. These large refineries are also the most integrated ones in terms of the number of processes used. The group of small refineries represents 67.1 percent in terms of numbers, but only 19.5 percent of the total crude capacity.

Classification of existing refineries as representative of older, typical, and newer technologies was based on the previously-mentioned Oil and Gas Journal survey of 1967. Since this survey included subprocesses as well as fundamental processes it provides good basic data for such a classification. However, numerous overlapping and single-purpose situations required considerable exercise of judgment in assigning specific refineries to one of the three classifications. The following examples illustrate the rationale of assignment. A relatively complete refinery that included both hydrocracking and isomerization was classified as "newer". A refinery with Thermofor catalytic cracking and polymerization but with neither alkylation nor hydrotreating was classified as "older". In many instances, particularly among the smaller refineries, the number of missing processes was so high that meaningful technological classification was not possible, and only 196 of the 261 refineries were classified. The remaining refineries were divided between the older and typical technologies with a bias toward the older, because the hard-to-classify, very small refineries are also the least likely to keep pace with general technological advance.

WASTE QUANTITIES AND CHARACTERISTICS

General Considerations

The next step after developing an understanding of the processing patterns and inter-relationships is to determine the wastewater quantities and characteristics and present them in a manner that will enhance interpretation of the pollution profile. If unit waste loads could be developed for each sub-process, then the current profile could be obtained by simply adding the components, and the future could be ascertained by projecting the types and sizes of refineries. However, the information required for such a direct approach is not available. Much of the available data on refinery wastes (whether from published sources or in the files of individual refineries) apply to total effluent, or major geographical sections of a refinery, rather than to specific processes. While the industry has been definitely interested in pollution abatement for many years, the investigative and corrective effort has been devoted mainly to effluent treatment and general improvement of in-plant operating practices without much quantitative in-plant evaluation. There has been little systematic effort to determine wastewater flows and characteristics for specific processes or operating units, and some of the available information of this type is quite old and of limited value for use at this time.

The wastewater information that is available for specific refinery subprocesses generally consists only of concentrations of pollutant materials and seldom includes wastewater volumes or operating capacity of the subprocess involved. In part, this circumstance results from the difficulty involved in obtaining representative samples. In many refineries, especially older ones, it is difficult even to find a place to take a wastewater sample, and it is even more difficult to find a location for accurate measurement of the wastewater flow. A further complication is the frequent occurrence of oil floating on the surface of the wastewater stream, which also interferes with the attainment of a representative sample.

Another factor restricting the application of a direct subprocess unit waste load approach is the frequent practice of combining specific waste streams discharging from several subprocesses rather than from specific units. Thus, such streams as sour waters, caustic washes, etc. in actual practice are generally not traceable to a specific sub-process, but only to a stripping tower or treatment unit handling wastes from several subprocesses.

The size, sequence, and combinations of contributing processes are so involved that a breakdown by subprocess would be extremely difficult to achieve.

In light of the above limitations, a rational approach has been developed. This starts with a qualitative evaluation of the principal refinery wastewater characteristics and the problems attributable to specific fundamental processes and waste streams; then the relatively meager quantitative wastewater information that is available is applied and apportioned in order to determine quantitative waste loadings for refinery processes.

Discussion of Pertinent Wastewater Characteristics

In view of the difficulty of determining definitive waste loadings for all parameters from each unit process, it is possible to present only limited quantitative information. However, considerable knowledge is available that can be used to make meaningful qualitative interpretations. Such information is presented in Table 3. This is a semi-graphic table with major waste-contributing fundamental processes shown with 3 X's, moderate contributors 2 X's, and minor contributors only 1 X. The table is based on pounds per day of contaminants from each fundamental process in a typical refinery, with throughput of each fundamental process taken into consideration.

The quantities and characteristics of the wastewater differ considerably for different processes. In general, the major sources of waste contribution are storage tank drainoffs, crude desalting and distillation, and the thermal and catalytic cracking processes, followed by the solvent refining, dewaxing, and drying and sweetening. A more detailed description of the sources and contaminants within the individual processes are presented as part of the description of fundamental processes in Appendix F.

Two significant general waste streams are the sour waters (containing sulfides and mercaptans) and the spent caustics. The sources of sour waters are primarily condensates from various fractionation units. Caustics originate from caustic washing (of feedstocks and intermediate and final products) to neutralize acidity and remove sulfides and mercaptans.

The general type and degree of sophistication of refinery wastewater treatment processes have been determined principally by the quantities and characteristics of total effluent, not by the configuration of refinery equipment or processes. The increasing stringency of pollution regulations requires consideration of wastewater treatment in terms of specific pollution problems. For this reason, a qualitative discussion of problems by individual parameter will be presented below. Appendix D is an interpretation of the significant water quality criteria, and these will be related to petroleum refining problems in the following discussion.

Flow

Based on total water usage, crude oil distillation is the largest water user mainly because of the large volumes required by the barometric condensers and desalters. Catalytic Cracking and Drying-and-Sweetening are the next largest water users. The extent of water use is significantly affected by the technology level of the processes employed. In newer plants, drastic reductions in water use are foreseen for Dewaxing, Alkylation, and Catalytic Cracking, primarily through increased water reuse.

Temperature

Crude desalting, especially the electrostatic process, contributes substantial thermal waste loads, as do distillation and cracking. The increased use of cooling towers has played an important role in the reduction of total thermal load primarily by reduction in quantities of water discharged and not necessarily by reduction in effluent temperature. Effluent heat loads can have significant adverse effects on the receiving waters since the increased temperature causes decreased oxygen solubility and greater oxygen utilization, both of which reduce the ability of the stream to handle waste loads.

pH

pH indicates the hydrogen ion concentration of a wastewater. However, the extreme values often observed do not truly reflect the buffering capacity of a waste or its ultimate effect upon a receiving water course. Most refinery wastewaters are alkaline, with the cracking (both thermal and catalytic) and crude desalting processes as the principal problem sources; some solvent refining processes also contribute substantial alkalinity. Power house boiler treatment produces alkaline wastewaters and sludges; hydrotreating, which is becoming increasingly important, contributes definite alkaline wastes. Alkylation and Polymerization utilize acid processes and have severe acidity problems. In general, petroleum refinery effluents have pH variations, but this is not a major problem from the standpoint of effluent standards. Where pH range is outside the normal limits, equalization of caustic wastes (and sometimes acid wastes) before bleeding into the sewer system is usually sufficient to maintain pH control. In general, large volumes of cooling and wash waters dilute out strong acid or caustic discharges; thus, pH may become a more significant problem as cooling water volumes decrease.

pH control is also important in regard to refinery wastewater treatment operations. Very low or very high pH can cause or worsen emulsification of oils already in the sewer. The pH of the wastewater influent to biological treatment processes, which are expected to be used to a much greater extent in the future, is an important consideration for effective treatment.

Oxygen Demand

The measurement of the biological and chemical demand an effluent will exert on the oxygen resources of a stream is a very meaningful water quality parameter. COD (chemical oxygen demand) and BOD (biochemical oxygen demand) are standard analyses used in this evaluation.

Almost without exception, wastewaters from petroleum refineries exert a major, and sometimes severe, oxygen demand. The primary sources are soluble hydrocarbons and sulfides. The combination of small leaks and inadvertent losses that occur almost continuously throughout a complex refinery can become principal pollution sources. Crude and product storage and the product finishing operations are the major contributors of COD and BOD, mainly because of the many tanks and vessels used, and the number of times a barrel of oil or product is handled in these operations. The wastewater discharges from these operations are intermittent. The cracking and solvent refining processes are the major BOD contributors on a continuous basis.

Phenol

Catalytic cracking, crude oil fractionation, and product treating are the major sources of phenolic compounds. Catalytic cracking produces phenols by the decomposition of multi-cyclic aromatics, such as anthracene and phenanthrene. Some solvent refining processes use phenol as a solvent, and although it is salvaged by recovery processes, losses are inevitable. Phenols, particularly when chlorinated, cause taste and odor problems in drinking water.

Sulfide

Sulfide waste streams generally originate from the crude desalting, crude distillation, and cracking processes. Sulfides herein discussed are considered to include mercaptans also. Sulfides interfere with subsequent refinery operations and are removed by caustic or diethanolamine scrubbing or appear as sour condensate waters in these initial processing operations. Hydrotreating processes which are used to remove sulfides in the feedstocks naturally produce a rich sulfide waste stream; however, most of the sulfide is removed as H_2S and is usually recovered or burned with the resultant SO_2 going to the atmosphere.

Oil

This is a major pollutant characteristic of refinery wastewaters. As free oil, it produces oil slicks and iridescence and coats boats and shorelines if permitted to discharge to the receiving stream. Stream and effluent discharge standards severely limit such discharges. Oil-coated solids are particularly troublesome since they are usually of neutral specific gravity, and are not readily removed by conventional gravity-separation techniques. Oil or oil-coated solids in the receiving stream also may have a serious detrimental effect on the aquatic life. Oil removal (in API separators or other facilities) is a necessary pretreatment step for biological waste treatment.

Oil has limited solubility in water and therefore would be expected to contribute little to effluent BOD or COD. However, crude petroleum and its refined products contain a wide range of soluble hydrocarbons which can ultimately find their way into waste streams through product washes, etc. These product wash streams contribute to effluent BOD and COD.

Quantitative Evaluation of Waste Loads

Basis of Evaluation

In view of the limitations imposed by the scarcity of wastewater data for specific subprocesses, the quantitative evaluation is based on apportionment of total refinery effluent data to supplement the incomplete specific subprocess effluent data. As a preliminary to discussion of this procedure, certain problems involved in the analysis of phenol and sulfide data should be reviewed. Determination of the quantities of phenols and sulfides being discharged from a process is difficult because the concentrations of these substances in the waste stream vary with conditions in the stream. If there is turbulence in the sewer phenols are extracted by the oil, and when the oil is skimmed off the phenols go with it. Thus, if the remaining waste is analyzed for phenols, a low concentration is measured. The sulfide concentration in the waste is affected by turbulence and changes in temperature and pH; increases in turbulence and temperature and a decrease in pH all act to liberate sulfides from the waste stream.

Wastewater surveys from only five refineries (3, 25) had pollutant concentration and wastewater flow data suitable for determination of waste loadings from individual subprocesses. Of these refinery surveys, one was very complete, three were fairly complete, and one was applicable to only a few subprocesses. None of these surveys gave the operating capacities of the subprocesses discharging the waste; this information was obtained from other sources (11, 13, 20). There was some question about several of the waste streams sampled being representative of all the waste coming from the particular subprocess in question. In other instances, there was reason to believe that the samples were collected after the waste stream had undergone some form of sour water stripping at the processing unit.

Because of the limited amount of data available, breakdown of waste loading on a subprocess basis was considered impractical and of doubtful validity. Therefore, the pollutant waste loadings and wastewater quantities are presented on the basis of fundamental processes without any further allocation to specific subprocesses. The original plan was to develop waste quantites and pollutant loadings for small, medium, and large refineries for each of the three levels of technology - older, typical, and newer. However, since the overall data source did not include all size ranges of refineries in each technology category, the original scope of presentation was reduced. The major difficulty was lack of data for establishing a relationship between refinery size and waste loadings. Thus, a hypothetical 100,000 bpsd refinery was selected as the basis for quantitative waste evaluation. This provides a reasonable evaluation of the effects of degree or level of technology on wastewater quanties and characteristics.

Based on the data from the five refinery surveys and supplemental pollutant concentration data from various published sources (5, 26, 27, 28, 29, 30), waste loadings and wastewater volumes per unit of process capacity were estimated for each fundamental process for which data was available. The division between older, typical, and newer was a difficult decision. One of the waste surveys available was definitely from an older refinery, and this was the major source of data for the older technology. The remaining surveys were from refineries in the typical class with only a few "newer" processing units in use. The waste loadings from these newer units in several refineries were used as the basis for estimating waste loadings and wastewater flows in a newer refinery. Throughout this estimating procedure there was a trend toward reducing waste loads as technology advanced from older to newer. This trend was substantiated by data available on total refinery effluents from older, typical, and newer refineries.

Waste Loads by Refinery Technology Level

Table 4 presents estimates of wastewater volumes and waste loadings for three of the major waste characteristics present in refinery effluents - BOD, phenol, and sulfides. These three characteristics, along with oil, are the major determinants of treatment requirements. It is realized that, in a refinery, the amount of oil in the wastewater is a major factor, but data concerning the amount of oil lost to the sewer from specific processes are not complete enough to justify inclusion of oil estimates in Table 4. Volumes and quantities are given for most of the fundamental processes for each of the three technologies. The processes for which data are severely limited are the ones at the tail end of integrated refineries; even when waste data was given, it was not complete in terms of concentration, flow, and process capacity. Since only a relatively few refineries manufacture asphalt, wax, and grease, etc., data on these fundamental processes are severely limited.

The values in Table 4 were determined by taking the volume or quantity of waste per unit of process capacity for each technology and multiplying by the capacity of that process in an older, typical, or newer refinery. An estimate of the total refinery effluent as sampled after an API separator is also given for each technology in Table 4. The estimate of total effluent was made for waste quantities after the API separator because that is where all refineries sample their plant effluent, and thus all the available effluent data is for such a sampling point. Prior to the API separator the free oil concentration is high, and this oil layer makes representative sampling difficult. These estimates of total plant effluent characteristics after the API separator are more reliable than the estimates of waste characteristics from each fundamental process because more data were available. This is so even though each of the refineries used differnet process series and efficiencies of the API separators vary.

Table 5 presents the same basic information as Table 4, except that waste quantities and volumes are presented on the basis of unit throughput instead of on the basis of crude charge to the refinery. This Table illustrates which fundamental processes (like polymerization) are particularly dirty, even though they do not contribute a large total waste loading in the typical refinery.

Table 6 is a summary of wastewater flow, and BOD, Phenol, and Sulfide waste loads for the overall effluent from older, typical, and newer refineries. These data (presented both as gallons or pounds per barrel of crude throughput, and as gallons or pounds per day for a 100,000 bpsd refinery) are based on measurement and analysis of the total refinery effluent after the API Separator of various refineries. This Table shows significant reductions in wastewater flow and in each of the listed pollutant characteristics from the older to the typical refinery and further reductions from typical to newer refinery. In the development of this summary, possible effects of refinery size on wastewater volumes and waste loadings were investigated; but no significant trends were detected. A recent published study of water use in petroleum refineries (9) supports this finding; this report states in part, "....that the unit make-up water requirements of the refineries surveyed were not directly affected by size."

Table 6 also includes a summary of wastewater volumes and waste loadings based on the fundamental process waste load data of Table 4. Comparison of this summary with the corresponding data based on total refinery effluent reveals some discrepancies. The wastewater flow based on total effluent is somewhat higher than the sum of the flows from the individual processes; the difference probably is a measure of the wastewater flow from the processes for which data was not available, and is an indication of variations in cooling water practices.

The BOD waste load in each case is also higher in the total effluent summary, particularly for the older and typical technologies. Actually the BOD loading not accounted for by fundamental processes is even greater than indicated in this table, because some BOD is removed in the API Separator. The unaccounted-for BOD probably comes from the fundamental processes noted on Table 5 as having insufficient data for waste load estimation, and from leaks, spills, and other non-process sources. The much smaller discrepancy (approximately 20 percent) for the newer refinery, where equipment, controls and operating procedures are likely to be superior, indicates the non-process sources as the major explanation of the discrepancy.

The summation of sulfides, on the other hand, exceeds the amount of sulfides present in the effluent for each technology. There are two reasons for this apparent discrepancy. First, as previously mentioned, the sulfides concentration will tend to decrease in the sewer as turbulence and temperature inrease and the pH decreases. Second, sour water strippers at various processing units remove some sulfides before the waterwater gets to the sewer.

Similarly, the phenol waste loads obtained by summation of wastes from the fundamental processes exceed the phenol measured in the plant effluent after the API Separator. This is because oil extracts phenol, which is then removed with the oil in the API Separator.

Waste Loads Per Unit of Product

Estimates of the total waste and wastewater quantities per unit of physical product for each of the three technologies are given in Table 7 for 14 petroleum products. The estimates were made by dividing the wastes from each fundamental process on the basis of the part that the process plays in the production of each of the 14 products. For example, a unit such as crude oil desalting or crude oil fractionation affects all 14 products. The wastes from each of these processes were then divided among each of the products of the basis of average yield of that product from a unit of crude oil throughput. On a national basis approximately 47 percent of refinery output is gasoline, 23 percent is furnace oil, 6 percent jet fuel, etc. Thus 47 percent of the wastes from crude distillation and crude desalting were assigned to gasoline, 23 percent of the wastes were assigned to furnace oil, 6 percent to jet fuel, etc. For a process such as dewaxing, the waste was divided only among the three products that result from dewaxing: 60 percent to lubricating oil, 30 percent to wax, and 5 percent to greases.

The division of each fundamental process into product segments was made using the product mix of refineries on the national level (17) and the predicted yields from each fundamental process as given in the literature (1, 2). The following factors were excluded in making the divisions, because they were considered to have either negligible or compensating effects:

1. Product yields vary with the type of crude oil.
2. Different refineries are operated for different product yields.
3. Product yields vary with the subprocess used.

After a certain percentage of the waste loads and wastewater volumes from each fundamental process were assigned to a product, the actual quantity or volume of waste was calculated by multiplying the percentage by the waste load in Table 4 for each fundamental process and technology. For example, 10 of the fundamental processes in an older refinery affect gasoline production. Gasoline production was ultimately a portion of each process's output and these percentages had been assigned. The percentage for each process was multiplied by the wastes from each process as given in Table 4. The resulting values were then totaled and taken as the total volume of wastewater and waste load resulting from gasoline production in a 100,000 bpsd older refinery. The waste loading per unit of gasoline produced was obtained by dividing the total quantity of each characteristic by the volume of gasoline produced by the hypothetical refinery, 47,000 bpsd. This procedure was repeated for each of the 14 products and each technology to obtain the values presented in Table 7.

These estimates of total waste and wastewater quantities are not complete, because the wastes from six fundamental processes are not given in Table 4. Nor do values in Table 7 include the unaccounted-for portion of the wastes as indicated in Table 4. These omissions must be kept in mind when comparing the wastes per unit of product. For example, asphalt is shown with low waste production per unit of product probably because the wastes from Blending and Packaging and Deasphalting are not included. The five other missing processes probably would not change the relative position of each product in terms of wastes generated per unit of product.

Another thing to consider when comparing the estimates in Table 7 is the volume of each product. The very low-volume items, such as greases, generate large amounts of wastewater and BOD per unit of product mainly because they are low-volume products rather than because the processes are high waste producers. Because of their low output, these products account for only a minor share of the total refinery waste load.

Some products, of course, produce more wastes than others per unit of product, but is difficult to make fair comparisons on this basis. In one sense all the products in a refinery other than gasoline can be considered byproducts of gasoline production. In that sense the wastes from gasoline production are being processed and sold as a product rather than being put into the sewer as may have been the practice 30 years ago. Each year petroleum refineries get more and more product volume per unit of crude processed.

These "byproducts" of gasoline production often contain wastes from gasoline production that must be removed from the "byproduct", and this often causes the "byproduct" to have a high waste generation per unit of product. For example, liquified petroleum gas (LPG) processing results in a large amount of sulfides being discharged to the sewer or burned. These sulfides come from the hydrogen sulfide that is released along with propane, butane, and other gases during distillation and cracking operations which play a large role in gasoline production. However, most of the hydrogen sulfide does not enter the environment until the gases given off during distillation and cracking are treated for removal of the hydrogen sulfide and production of LPG.

Projected Gross Waste Loads

An estimate of the 1963 industry-wide waste loads and wastewater volumes following the API Separator is given in Table 8, along with projections of the loads and volumes through 1977. The 1963 estimates for wastewater volume and BOD, phenol, and sulfide loadings were made using the unit waste loadings for a typical technology as given in Table 6. These waste loadings per unit of crude capacity were multiplied by the industry's crude capacity in 1963, 10.45 x 10^6 bpsd (13), to obtain the total daily waste loadings. It was felt that the accuracy of the estimates for each technology in Table 6 was not good enough to justify determining the total waste loading by adding the waste loads from each technology on the basis of the crude capacity of each technology. Therefore, the unit waste loading of the typical technology was used. Any error resulting from this simplified approach is reduced by the fact that the higher waste loadings from an older technology and the lower waste loadings from a newer technology tend to cancel each other.

The projected waste loads and wastewater volumes given in Table 8 were obtained using an annual rate of increase of approximately 3.6 percent for waste loads and an annual increment of 10,000,000 gallons of wastewater volume. This annual increase gives 50 percent increase in total industry waste loading between 1963 and 1977. The 3.6 percent per year figure was obtained by projecting several parameters including crude capacity, crude throughput, and product value added. Waste load projections based on crude capacity have the advantage of the availability of reliable information on crude capacity. This information indicates an increase of 17 - 20 percent from 1963 to 1967. On the other hand, the relationship between waste loads and crude capacity may change from year to year, as the extent to which the capacity is utilized changes. Thus, crude oil throughput would be a more meaningful projection basis than crude capacity. Extrapolation of 1959 - 1965 records of crude throughput in U. S. refineries indicated a 38 percent increase between 1963 and 1967.

The third projection basis, product value added, is somewhat more complicated in the calculation of the product value trend, but overall is probably the most logical projection basis. The total waste loads and wastewater volumes for 1963 can be determined with a good degree of confidence from the unit loadings by fundamental processes. The projections to 1977 can be made by forecasts or by extrapolation of past and current product values. Two groups of statistics are available for determining product value: "value added by manufacture", which reflects labor, material, packaging and related costs; and "value of shipments", which includes the value added, plus costs for raw materials, transportation, etc. Straight-line extrapolation of 1950 - 1964 data indicates increase of 42 and 83 percent from 1963 to 1977 for value of shipments and value added by manufacture. An alternative product value projection method is the multiple regression method of the Business and Defense Administration of the U. S. Department of Commerce, based on Gross National Product, Gross Private Business Investments, and other economic components. This produces a projection of 88 percent increase in product value added between 1963 and 1977, using a rather liberal 6 percent annual increase in GNP.

By the various methods of projection the waste load increase between 1963 and 1977 could be 17 to 88 percent. A 50 percent increase was selected as a reasonable compromise between the crude throughput increase of 38 percent and the BSDA value added increase of 88 percent. Wastewater volume increase was estimated to be much lower than the waste loading increase because of significant developments in cooling water practices.

Seasonal Waste Production Patterns

Seasonal waste production patterns can be established by variations in output of specific products through the calendar year. The petroleum refining industry experiences only slight changes in product mix through the year, and total production does not change significantly. The most noticeable variation in product demand is that of distillate fuel oil. The total demand for it during the winter months of December and January is more than twice the demand during June and July. The peak demand for gasoline occurs during the summer months, and this demand is approximately 20 percent higher than the demand during January and February. However, these fairly large variations in demand are not reflected in production patterns primarily because of product inventory practices and the increasing distillate fuel-gasoline flexibility of the catalytic cracking processes.

Table 9 gives a monthly breakdown of total crude throughput and gasoline and distillate fuel oil production for 1964 and 1965. These figures show that there is only a 17 percent difference in distillate fuel oil production between the highest and lowest month. The maximum variation in gasoline production was about 15 percent. The volume of total crude throughput is perhaps the best method of predicting any changes in waste'production, and its maximum variation is only 13 percent. On any of these bases, Table 9 indicates that there is no appreciable seasonal waste production pattern.

WASTE REDUCTION PRACTICES

In-Plant Processing Practices

A complete evaluation of the effectiveness of in-plant processing practices in reducing wastewater pollution requires detailed information on the wastewater flows and pollutant concentrations from all types of refinery processing units and storage facilities. With such information one could determine the pollutional effect of substitution of one alternative subprocess for another, or of improvement in general operating and housekeeping practices. Unfortunately, this kind of information is not available, nor does there appear to be any systematic effort, even in the latest installations reflecting the newest technology, to determine waste loads from specific units.

Despite this lack of specific process wastewater data, there is information of a more general nature which indicates substantial wastewater pollution reduction through changes in processing facilities and practices. Hydrocracking and hydrotreating are two processes that generate much lower waste loadings than the processes they are replacing. The rapid pace at which such units are being installed is exerting and will continue to exert a strong influence on the reduction of waste loadings, particularly sulfides and spent caustics.

However, the greatest potential for waste reduction by in-plant processing changes appears to be in improvement of general operating and housekeeping practices rather than in changing processes or subprocesses. For example, substantial reductions in losses of oil to the sewers could be achieved through improvement of current practices in taking samples of charge stocks and products and in drawing off water from storage tanks. Another general indication of significant pollution reduction by in-plant measures is afforded by the lower pollutant loads per unit of through put or product for refineries in the newer technology category as compared to typical or older refineries. Undoubtedly some of this reduction results from newer subprocesses, but much of it also appears to come from better controls, improved operating and sampling practices, and similar general considerations.

Waste Treatment Practices

Discussion of Pertinent Waste Treatment Processes

Gravity Separation

Gravity separation to remove oil is the first step in the treatment of refinery wastes. The functioning of gravity-type separators depends upon the difference in gravity of oil and water. The gravity-type separator will not separate substances in solution, nor will it break emulsions. The effectiveness of a separator depends upon the temperature of the water, the density and size of the oil globules, and the amounts and characteristics of the suspended matter present in the waterwater. The "susceptibility to separation" (STS) test is normally used as a guide to determine what portion of the influent to a separator is amenable to gravity separation.

The Gravity Separator usually consists of a pre-separator (grit chamber) and a main separator, usually rectangular in shape, provided with influent and effluent flow distribution and stilling devices and with oil skimming and sludge collection equipment. It is essential that the velocity distribution of the approach flow be as uniform as possible before reaching the inlet distribution baffle.

Gravity-type separators are used by all refineries to remove free oil from oil-containing wastes. The oil skimmed from the separator is processed to recover the oil, and any sludge which settles can be dewatered and either incinerated or disposed of as landfill.

Dissolved Air Flotation

Dissolved air flotation consists of saturating a portion of the wastewater feed or a portion of recirculated effluent from the flotation unit with air at a pressure of 40 to 60 psig. The wastewater or effluent recycle is held at this pressure for 1 - 5 minutes in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles in the wastewater in the flotation chamber. This results in agglomerates which, due to the entrained air, have greatly-increased vertical rise rates, of about 0.5 to 1.0 feet/minute. The floated materials rise to the surface to form a froth layer. Specially designed flight scrapers or other skimming devices continuously remove the froth. The retention time in the flotation chambers is usually about 10 - 30 minutes. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. The attraction between the air bubble and particle is a result of the particle surface and bubble-size distrubtion.

Chemical flocculating agents, such as salts of iron and aluminum with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification of refinery effluent.

Dissolved air flotation is used by a number of refineries to treat the effluent from a gravity separator. Dissolved air flotation using flocculating agents is also used to treat oil emulsions. The froth skimmed from the flotation tank can be combined with other sludges (such as those from a gravity separator) for disposal. The clarified effluent from a flotation unit may receive further treatment in a biological unit or may be discharged as final effluent, depending on the BOD content and effluent requirements.

Activated Sludge Process

Activated Sludge is an aerobic biological treatment process in which high concentrations of newly-grown and recycled microorganisms are suspended uniformly throughout a holding tank to which raw wastewaters are added. Oxygen is introduced by mechanical aerator, diffused air systems, or other means. The organic materials in the waste are removed from the aqueous phase by the microbiological growths and stabilized by biochemical synthesis and oxidation reactions. The basic activated sludge process consists of an aeration tank followed by a sedimentation tank. The flocculent microbial growths removed in the sedimentation tank are reycled to the aeration tank to maintain a high concentration of active microorganisms. Although the microorganisms remove almost all of the organic matter from the waste being treated, much of the converted organic matter remains in the system in the form of microbial cells, which have a relatively high rate of oxygen demand and must be removed from the treated wastewater before discharge. Thus, final sedimentation and recirculation of biological solids are important elements in an activated sludge system.

Sludge is wasted on a continuous basis at a relatively low rate to prevent build-up of excess activated sludge in the aeration tank. Shock organic loads usually result in an overloaded system and poor sludge settling characteristics. Effective performance of activated sludge facilities requires pretreatment to remove or substantially reduce oil, sulfide (which causes toxicity to microorganisms), and phenol concentrations. The pretreatment units most frequently used are: gravity separators and air flotation units to remove oil; and sour water strippers to remove sulfides, mercaptans, and phenol. The high rate and degree of organic stabilization possible with activated sludge has already resulted in some application of this process to the treatment of refinery wastewaters, and the extent of use is expected to increase.

Trickling Filter

A trickling filter is an aerobic biological treatment process with a fixed growth of microorganisms contained in a porous bed, through which the wastewater is passed. A microbial film develops on the surface of the bed media and removes organic materials from the wastewater by adsorption, bioflocculation, and sedimentation. Oxygen is very important in the trickling filter system (as in any aerobic biological system) for rapid metabolism of the removed organic matter. The large surface area of the filter media permits rapid transfer of oxygen by simple diffusion from the void spaces into the liquid layer. Treatment rates on trickling filters are controlled by hydraulic as well as organic loading rates. Trickling filters with stone media are limited by economics to depths between 3 feet and 10 feet. Plastic, rather than rock, media are generally used in filters which have very high hydraulic and organic loadings, with bed depths approaching 40 feet.

Trickling filter units have been used in the petroleum industry both as complete secondary treatment and as roughing devices to reduce the organic load on subsequent activated sludge units. The trickling filter is extensively used to remove phenolic compounds, and has been used to treat sour waters.

The wastewater applied to the filter normally requires pretreatment to remove oil, and to limit concentrations of sulfides, mercaptans and phenol; oil removal is accomplished by gravity separation and air flotation, and sulfide and mercaptan removal is accomplished by stripping.

Aerated Lagoon

An aerated lagoon provides aerated biological treatment by mixing dilute concentrations of microorganisms with wastewater in a large, relatively deep basin. Oxygen necessary for aerobic stabilization of organic matter is supplied by mechanical or diffused aeration units, and by induced surface aeration. The turbulence normally maintained in the basin insures distribution of oxygen and biological solids throughout the basin.

An aerated lagoon differs from an activated sludge unit in that the effluent from the aerated lagoon is not settled prior to discharge, and the biological solids are not recirculated. Because of the low rate of organic removal resulting from the low concentration of biological solids maintained in the system, aerated lagoon detention time (and basin volume) is greater than in an activated sludge system for removal of an equivalent amount of BOD. An aerated lagoon is capable of removing 55-90 percent of applied BOD, depending on wastewater temperatures and treatability.

Oxidation Pond

The oxidation pond is useful as a biological treatment system where land is plentiful and cheap. Fundamentally, the oxidation pond utilizes bacteria to aerobically stabilize the organic wastes added to the pond. Oxygen for the bacteria is supplied by atmospheric reaeration at the pond surface and from oxygen production by algae in the pond. The production of oxygen by algae occurs as a result of synthesis of cellular protoplasm from carbon dioxide in the presence of sunlight. The organic loading on the oxidation pond is limited by the lack of mixing, which also limits the oxygen transfer capacity. In heavily loaded ponds a certain amount of the stabilization will occur anaerobically rather than aerobically. Temperature plays an important part in the efficiency of oxidation ponds, especially if the ponds are loaded to near capacity. Turbidity, colored wastes, and emulsions block part of the light transmittance and reduce the production of oxygen by algae. Because organic loadings are low, very little biological sludge is produced; what little is produced settles in the pond.

Oxidation ponds have been used as the only treatment of refinery waste and also as a polishing step for the effluent from physical-chemical or other biological waste treatment processes. Multi-cellular ponds are used in some instances, especially if the oxidation pond is used as a basic treatment unit rather than a polishing unit. The first pond generally functions as an emergency oil skimming pond and also serves to settle out heavy solids.

Pretreatment of wastewater is normally required before it can be treated in an oxidation pond. Pretreatment is carried out to remove oil, and to limit concentrations of sulfides, mercaptans and phenol.

Emulsion Breaking

This is used to remove oil from oil-in-water and water-in-oil emulsions. Oil emulsions may comprise several percent of refinery throughput and therefore represent an important economic consideration. Emulsions result from the intimate contact between oil, water, and emulsifying agents, or may originate directly as process byproducts.

Emulsions may be broken by electrical, chemical, or physical methods (heating, filtration, or centrifugation). In the electrical process, water-in-oil emulsions are passed through an electrical field to coalesce the water droplets sufficiently to produce gravity settling of the water phase.

In the chemical process both oil-in-water and water-in-oil emulsions can be treated. The process consists of rapidly mixing coagulating chemicals with the waste, followed by flocculation and flotation or settling. Acidification alone is also used. Settling usually results in separation of the aqueous layer. The recovered oil is skimmed for subsequent reprocessing.

Physical emulsion-breaking methods include heating, centrifugation, and precoat filtration. Emulsion breaking by heating markedly reduces the viscosity of the oil phase, permitting coalescence and separation of the oil and water phases to take place. Centrifugation breaks oil emulsions by separating the oil and water phases under the influence of centrifugal forces. Stable water-in-oil emulsions, particularly those stabilized by finely divided solids, can be broken by continuous precoat filtration. Emulsion breaking occurs as a result of rupture of the globules of the dispersed phase on passing though the interstices of the filter cake and precoat materials, and as a result of the removal of the stabilizing solids.

Treatment of Ballast Waters

Ballast water generally requires treatment for the separation of oil from wastewater. Ballast water oil can be present as free oil or as emulsified oil. Minimum treatment for ballast water involves settling the waste in storage facilities and skimming the oil. The settling tank can also be provided with a steam coil for heating the tank contents to help break emulsions, and an air coil to provide agitation.

Further treatment may consist of providing a coagulation or a chemically-aided air flotation unit to remove emulsified oil, or filtration to remove suspended particles and oil. The oil skimmed from various treatment units is discharged to a slop oil storage tank for further processing to recover the oil.

Spent Caustic Treatment

Alkaline solutions are used to wash refinery gases and light products; the spent solutions, generally classified as sulfidic or phenolic, contain varying quantities of sulfides, sulfates, phenolates, naphthenates, sulfonates, mercaptides and other organic and inorganic compounds. These compounds are often removed before the spent caustic solutions are added to refinery effluent. Spent caustics usually originate as batch dumps, and the batches may be combined and equalized before being treated and/or discharged to the general refinery wastewaters.

Spent caustic solutions can be treated by neturalization with spent acid or flue gas, although some phenolic caustics are sold untreated for their recoverable phenol value. Neutralization with spent acid is carried to a pH of 5 to insure maximum liberation of hydrogen sulfide and acid oils.

In the treatment of spent caustic solutions by flue gas, hydroxides are converted to carbonates. Sulfides, mercaptides, phenolates, and other basic salts are converted to hydrogen sulfide, phenols and mercaptans at the low pH conditions caused by the flue gas stripping. Phenols can be removed and used as a fuel or can be sold. Hydrogen sulfide and mercaptans are usually stripped and burned in a heater. Some sulfur is recovered from stripper gases. The treated solution will contain mixtures of carbonates, sulfates, sulfites, thiosulfates and some phenolic compounds. Reaction time of 16 - 24 hours is required for the neutralization of caustic solution with flue gas.

Sour Water Treatment

The purpose of the treatment of sour water is to remove sulfides (as hydrogen sulfide, ammonium sulfide and polysulfides) before the waste enters the sewer. The sour water can be treated by stripping with steam or flue gas, air oxidation to convert hydrogen sulfide to thiosulfates, or vaporization and incineration.

The heated sour water is stripped with steam or flue gas in a packed or plate-type column. Hydrogen sulfide released from the wastewater can be recovered as sulfuric acid or sulfur, or may be burned in a furnace. The bottoms have a low enough sulfide concentration to permit discharge into the general wastewater system for biological treatment. If the waste contains ammonia, it is neutralized with acid before steam stripping. The waste liquid passes down the stripping column while the stripping gas passes upward.

Another way of treating sour water is to oxidize by aeration. Compressed air is injected into the waste followed by sufficient steam to raise the reaction temperature to at least 190°F. Reaction pressure of 50-100 psig is required. Oxidation proceeds rapidly and converts practically all the sulfides to thiosulfates and about 10% of the thiosulfates to sulfates. Air oxidation, however, is much less effective than stripping in regard to reduction of the oxygen demand of sour waters, since the remaining thiosulfates can later be oxidized to sulfates by aquatic microorganisms.

In treating sour water by stripping and incineration, sufficient care must be taken to prevent an air pollution problem due to insufficient burning of sulfides removed from sour water. Hydrogen sulfide itself is a foul-smelling gas, and any releases to the atmosphere cause odor problems.

The removal of hydrogen sulfide and ammonia occur at different pH conditions. The removal of hydrogen sulfide requires a pH in the acidic range, while ammonia removal occurs in the alkaline range. The stripping of sour water is normally carried out to remove sulfides, and hence the effluent may contain 100 - 2000 ppm of ammonia depending on the influent ammonia concentration.

Slop Oil Treatment

Separator skimmings, which are generally referred to as slop oil, require treatment before they can be reused, because they contain an excess of solids and water. Solids and water contents in excess of about 1 percent generally interfere with processing.

In most cases slop oils are easily treated by heating to 190°F., retaining at this temperature for 4 to 6 hours, and then settling for 12 to 24 hours. At the end of settling, three definite layers exist: a top layer of clean oil; a middle layer of secondary emulsion; and a bottom layer of water containing soluble components, suspended solids and oil. In some cases it is advantageous or even necessary to use acid or specific chemical demulsifiers to break slop oil emulsions. The water layer resulting from acid and heat treatment has high BOD and COD and also high pH, and must be treated before it can be discharged.

Slop oil can also be successfully treated by precoat filtration. The normal precoat is diatomaceous earth.

Cooling Towers

Cooling towers are used in many refineries to dissipate heat from recirculated spent cooling water and thereby reduce water supply requirements. Cooling towers are not normally considered to be an effluent treatment device except that total effluent quantity is reduced by their use. However, cooling towers have been used to treat refinery effluents biologically where cooling water supply is short and it is economically advantageous to reclaim sufficient water to meet the cooling water makeup needs of the refinery.

In some cases, selected process waste streams are discharged to the cooling water system. In these cases the cooling towers act as a biological treatment system, in which oxygen is transferred by the air which cools the wastewater circulating through the cooling tower, and the excess biological growth is continuously discharged into the cooling tower blowdown. Some biological growths become attached to the cooling tower itself, but the quantity of adhered growth appears small. Normally the waste receives sufficient dilution in the recirculating water to prevent excessive growths, which can plug heat exchangers and pipelines.

Cooling towers handling restricted loadings of specific wastes are capable of 99 percent phenol removal, 75 - 90 percent COD removal, and 90 percent BOD removal. These percent removals include the effects of windage losses and volatilization, as well as biological effects. With proper control, heat transfer capacity is not appreciably affected by increased biological growths formed through the use of wastewater in cooling towers, although operating effort may be increased. One of the benefits of using wastes as partial makeup is that the oxygen demand of the wastewater reduces the concentration of dissolved oxygen in the cooling water and thus tends to reduce corrosion of steel and cast iron.

Pretreatment of waste may be required before it can be used as makeup water for cooling purposes. Oil-bearing waste must pass through a gravity separator to remove oil, and other process wastes may require treatment in a stripper to remove sulfides and mercaptans.

Disposal of Steam Generation Wastes

Steam is required for many refinery processes and usually is generated on site; the current trend is to waste heat boilers at processing units rather than major dependence on centralized boiler houses. Water for steam generation must be exceptionally pure to avoid excessive scaling and corrosion of boiler tubes. Consequently, boiler feed water is treated mainly for removal of solids and alkalinity; this produces an alkaline sludge. Other sources of waste are the continuous boiler blowdown required to control the dissolved solids concentration in the boiler water, and intermittent blowdown of sludge which accumulates in the boiler.

The boiler blowdown water, relatively high in solids and alkalinity, is almost always discharged directly to the refinery sewer system. The feedwater treatment sludge is also discharged to the sewer, although in some cases other disposal methods are used. Some refineries lagoon the sludge, and others use it to neutralize acid wastes or for coagulant purposes. In general the boiler blowdown constitutes only a small part of the overall refinery wastewater, but the solids and alkalinity may reduce the effectiveness of oil removal in the separators.

Sludge Disposal

Sludges from refinery operations and waste treatment processes can be handled in a number of ways. Historically, the method first used was lagoon storage of sludges in vacant areas of the refinery, with ultimate disposal of the combustible materials by open burning. As land becomes scarcer, it becomes more important to concentrate the sludges prior to disposal.

Methods of sludge concentration vary with the type of sludge. Oily sludges such as storage tank and gravity separator bottoms can be concentrated by precoat vacuum filtration or centrifugation. It is possible to recover a certain amount of oil from the sludge by these methods.

Sludges from boiler treatment blowdown and chemical or biological treatment of refinery effluents can be thickened and subsequently dewatered by vacuum filtration or centrifugation. Ultimate disposal of dewatered sludge can be by incineration, landfill or ocean disposal. Acid and caustic sludges from refinery processes generally require neutralization before dewatering and ultimate disposal.

Effectiveness of Waste Removal

A summary of the effectiveness of waste treatment processes in removing the principal oil refinery pollutants is presented in Table 10. For convenience of discussion, the treatment methods have been divided into 5 generic types: Physical, Chemical, Biological, Tertiary, and In-plant. Included as a parameter in the table is the Most Probable Process Influent (MPPI), which indicates the kind and/or extent of prior treatment required for efficient utilization of the specific process under consideration.

In addition to removal efficiencies for specific pollutants, the summary includes qualitative information on the effect of the various treatment processes on three important general pollutional characteristics: pH, toxicity, and temperature. The removal efficiency ranges and the qualitative effects are based on available data from actual refinery installations; however, considerable exercise of engineering judgment based on general wastewater treatment experience was required to supplement the relatively meager data in several areas.

Physical Treatment

Included in this type of treatment are gravity separators (API and earthen basins), evaporation, and air flotation without chemicals. Gravity separators are designed primarily for removal of floatable oil and settleable solids, and they achieve removals of 50-99 percent of separable oil and 10-85 percent of suspended solids. Concurrent with these major functions, gravity separators also remove BOD, COD, and at times phenol: these removals can be substantial (up to 40-50 percent) depending on the characteristics of the waste. Phenols are oil-soluble and thus could be extracted from combined wastewaters and removed along with the oil by the separators.

The oil removal efficiency of gravity separators is greatly influenced by the quality of in-plant wastewater management, as well as by the design and operation of the separators themselves. Large amounts of separable oil in the wastewater system can be removed at high efficiency by the separators, but the effluent quality (which varies from 20 to 150 mg/L of oil) would be much better if effective in-plant controls had been used to minimize the amount of oil getting to the sewers in the first place. In addition, oil in the form of emulsions, and especially when coated on fine solids, is difficult to remove with gravity separators.

It should be noted that the BOD and COD removals shown in Table 10 for gravity separators do not include the BOD and COD attributable to the readily-separable oil which is removed. Inclusion of these would indicate unrealistically high organic removals that would be inconsistent with the quantities of contaminants actually dispersed in the wastewater.

The treatment of refinery effluents by evaporation is severely limited by geographical location, climate, and land availability. It is obviously a very attractive method where stringent effluent regulations are in force and the geographical, climatic and land conditions are favorable. At least one refinery in the continental U. S. utilizes this method. Pollutant removals are essentially complete. However, in order for this method to function, even where geographically feasible, extensive water reuse must be practiced.

Air flotation without chemicals, like evaporation, is not widely used in refinery waste treatment at the present time. In general the performance is comparable to gravity separators, but with somewhat better oil removal. In addition to those waste parameters where definite efficiency ranges are presented, an undetermined amount of sulfides will be oxidized by the oxygen dissolved from the applied air. Some stripping of ammonia may also occur if the pH is alkaline.

Chemical Treatment

Chemical methods of treating refinery effluents include chemical coagulation-sedimentation, and air flotation with chemical addition. Removal efficiencies of coagulation-sedimentation and chemically assisted air flotation are judged to be essentially the same. The chemical methods are more effective than gravity separators, particularly in regard to removal of emulsified oil; in addition, slightly more BOD (beside that associated with separable oil) will probably be removed by chemical coagulation then by air flotation.

As was the case with simple air flotation, it is likely that in chemical air flotation a portion of the dissolved sulfide will be oxidized and some ammonia stripped off by action of the entrained and released air.

Biological Treatment

Types of biological treatment used for refinery wastewaters include activated sludge, trickling filter, aerated lagoons and oxidation ponds. All of these treatment methods require prior removal of oil. A general comparison of the relative merits of the various biological methods and their applicability to different wastewater situations is available from the previous section of this report, **Discussion of Pertinent Waste Treatment Processes.**

Table 10 indicates that Activated Sludge is the most effective process for removal of organic materials, with removal efficiencies of 70-95 percent for BOD, 30-70 percent for COD, and 65-99 percent for phenols and cyanides. Suspended solids removal efficiencies are good, except with aerated lagoons. Since these lagoons are seldom followed by sedimentation facilities, it is entirely possible that the concentration of solids leaving the lagoons would be higher than that of the influent wastewaters.

In any biological treatment system there is a unique and important relationship between the ammonia and BOD concentrations in the wastewaters. The organisms which develop to oxidize the organic material will utilize approximately 5 pounds of ammonia nitrogen and 1 pound of phosphorus for every 100 pounds of BOD removed. These nutrients probably will not have to be added in a petroleum refinery treatment system, because there is almost always enough ammonia (from corrosion inhibitors) and phosphorus (from cooling tower blowdown) present in the refinery wastewater.

Acidity/alkalinity will be altered by the buffering action which accompanies the development of biological growths. This buffering is due primarily to the carbon dioxide formed during biological oxidation, which produces bicarbonates in the wastewater.

Tertiary Treatment

The treatment of secondary effluents in petroleum refineries has been limited to activated carbon and ozonation. The primary purpose of tertiary treatment is to remove refractory organics and small quantities of phenols which pass through biological treatment processes. Activated carbon and ozonation are very effective in removing these materials. Chlorination cannot be used for these purposes because of the formation of chlorophenols, which have highly objectionable taste and odor characteristics.

In-Plant Treatment

Major treatment processes which are applicable to individual process effluents or groups of effluents within a refinery are stripping of sour waters, neutralization and oxidation of spent caustics, ballast water separation, slop oil recovery, and temperature control. The particular areas of application of these processes have been covered in the previous Discussion of Pertinent Waste Treatment Processes.

Sour water strippers are designed primarily for the removal of sulfides and can be expected to achieve 85-99 percent removal. If acid is not required to enhance sulfide stripping, ammonia will also be stripped with the percentage varying widely with stripping temperature and pH. If acid is added to the wastewater, essentially none of the ammonia will be removed. Thus, ammonia removals in sour water strippers vary from 0 to 95 percent. Depending upon such conditions as wastewater pH, temperature, and contaminant partial pressure, phenols and cyanides can also be stripped with removal as high as 30 percent. COD and BOD are reduced because of the stripping out of phenol and oxidizable sulfur compounds.

The oxidation phase of spent caustic treatment is aimed at the sulfide content of these wastes and achieves 85-99 percent sulfide removal. In this process, sulfides are oxidized primarily to thiosulfates although in some variations there is partial oxidation of the sulfur compounds to sulfate. Oxidation processes are not applied to phenolic caustics because phenols inhibit oxidation. It should be noted that those processes which oxidize the sulfide only to thiosulfate satisfy only part of the oxygen demand of the sulfur, as thiosulfate can be oxidized biologically to sulfate. Neutralization of spent caustics is applied to both phenolic and sulfidic caustic streams; the sulfidic caustics are also steam stripped, after neutralization, to remove the sulfides. When phenolic spent caustics are neutralized, crude acid oils or "crude carbolates" are sprung and thus removed from the wastewater. The major part of the phenols will appear in the oil fraction, but a significant part may remain in the wastewater as phenolates.

Ballast Water Treatment, Slop Oil Recovery, and Temperature control are included in the list of In-Plant Processes, primarily for discussion purposes rather than evaluation as part of the overall refinery wastewater treatment system. Ballast water normally is not discharged to the refinery sewer system because the intermittent high-volume discharges, with potentially extremely high oil concentrations, would upset the refinery wastewater treatment facilities. Thus ballast waters are treated separately, with heating, settling, and at times filtration as the major steps. The recovered oil, which is considerable, is generally sent to the slop oil system.

Temperature control is becoming increasingly important as stream standards become more stringent. Reducing the heat load to the river without changing manufacturing processes is possible only by increased water reuse through cooling towers, spray ponds, or dry finned-tube air coolers. The heat load to the water course is reduced by the amount transferred to the atmosphere. It is conceivable that the temperature of the effluent in certain situations might be raised even though the total heat load is reduced. A number of refineries have made use of cooling towers as biological treatment processes, especially for phenol-bearing wastes.

Reuse or recovery of refinery process sludges has been discussed in a previous section. Process sludges and sludges produced in biological treatment of wastewaters are generally dewatered and burned or disposed of as landfill. The burning of sludges must be carefully controlled to prevent air pollution.

Rate of Adoption of Waste Treatment Processes

The estimated percentage of oil refineries using specific waste treatment processes is presented in Table 11. This table is primarily the result of judgment based on a relatively small sample of present refineries and expected trends. There is a dearth of usable information on the present waste treatment "mix" used by refineries. The most reliable data are for gravity separators; all refineries use some sort of gravity separation for removal of separable oil. Values were estimated for 1950, 1963 and 1967, and projected for 1972 and 1977.

The values shown for 1977 reflect the assumption of more comprehensive and more stringent water and air pollution regulations. In particular, it is assumed that 90 to 100 percent of the plants will be required to provide some type of biological secondary treatment. Processes such as incineration of spent caustics and flaring of stripped sulfides should be drastically reduced by 1977 as the result of air pollution requirements. The percentage of plants utilizing ballast water treatment was assumed to be equal to those receiving their supplies by tanker.

Sequence and Inter-relationships of Waste Treatment

The sequence of waste treatment required for refinery wastes due to various technological considerations is shown in Table 12. The treatment requirements are divided into 1) primary; 2) secondary; 3) tertiary; 4) pre-treatment; 5) disposal of sludges and slop oil emulsion; and 6) miscellaneous treatment. Whenever feasible, wastes should be separated at the source to avoid contamination of large volumes of uncontaminated waste streams such as cooling water.

In order to provide efficient treatment to the wastes originating within a refinery, it is very important that segregation of concentrated waste streams be considered. Segregation of waste streams frequently simplifies waste treating problems. Thus, treatment of highly polluted waste streams at the source can prevent gross pollution of large volumes of relatively clean wastewater. Such treatment is often a more economical solution of a problem than would be possible if wastes are discharged directly to the refinery sewers. Treatment at the source is also helpful in recovering by-products from the wastes which otherwise could not be economically recovered when the wastes are combined. Treatment at the source is useful not only for recovery of by-products but also for preparation of the wastes for subsequent treatment. For example, sour water and spent caustics which are treated biologically must be pretreated to remove sulfides and mercaptans, which are toxic to microorganisms present in the biological treament units. Segregation of relatively clean wastewater, such as cooling water, is helpful in reducing the total quantity of wastes to be treated, since cooling waters constitute such a large percentage of wastewater flow.

The wastes that normally receive secondary treatment are the oily wastes, sour water, and spent caustic. These wastes can be treated in one of several types of secondary treatment units. Occasionally, a combination of biological treatment units, rather than a single type of unit, is used in the petroleum industry. Trickling filters have been used to level out the organic load before the wastes are treated by activated sludge. Aerated lagoons and oxidation ponds in series are also used to treat the wastes, and cooling towers are sometimes used as biological treatment units for specific process wastes. The effluent from secondary treatment units can be further treated to remove organic matter, taste-and-odor producing substances, and dissolved inorganic substances. Treatment by oxidation with ozone is particularly useful in removing phenols from petroleum wastewaters. This is important when the effluent from petroleum refineries is discharged to natural bodies of water used as a source of water supply. Ion exchange can be used to remove inorganic substances from treated wastewater, but it is unlikely that such a high quality treatment will be required for refinery wastes. In the treatment of wastes, sludge and slop oil emulsions are produced and require treatment. The treatment required for sludge and slop oil emulsion is shown in Table 12. The solids resulting from these treatment processes are disposed of by either landfill or incineration.

There are several waste streams which do not require very extensive treatment. Cooling waters, which in general are relatively clean, can either be discharged directly to the receiving waters or (if they contain oil) treated in a gravity separator before discharge. Spent catalysts are not normally discharged to the sewer. They can either be regenerated for reuse, or disposed of as landfill. Spent catalysts like aluminum chloride and phosphoric acid must be neutralized before being used as landfill. Acid sludges can be treated to recover sulfuric acid or can be disposed of by incineration. Waste streams such as spent caustic or acid sludges can be concentrated and incinerated. Ballast waters are not normally discharged to oil sewers because of the large quantity of such wastewater. Ballast water can be treated in gravity separators to remove free oil, or by chemical flocculation if it contains oil emulsions. If further treatment with general wastewaters is indicated flow equalization is required.

There are several factors which may affect the treatment efficiency of different processes. Oil wastes should not be mixed with process wastes containing chemicals which tend to emulsify the oil and reduce the efficiency of gravity separators. Large amounts of oil tend to coat the microbial surface in a trickling filter, thus reducing the transfer of organic matter. In activated sludge, the oil causes the sludge to float in the sedimentation tank and to be lost to the effluent. As mentioned earlier, high concentrations of sulfides must be reduced in sour waters as they are toxic to the microorganisms present in the biological treatment units. In the stripping of sour water, pH is important in the removal of sulfides and ammonia. Stripping with flue gas causes the pH of wastewater to be in the acidic range, and ammonia may not be removed. In steam stripping considerable ammonia will be removed because the pH is not lowered by this treatment. The cost of secondary treatment will vary considerably depending upon the units used in secondary treatment. Activated sludge facilities are less expensive to construct but the operating costs will be high; on the other hand, a trickling filter for most refinery wastewater applications will probably be higher in capital cost but lower in operating costs. Pond treatment is economical only when sufficient land is available at low cost, but the operating cost will be very low compared to activated sludge or trickling filter. Treatment of wastes in cooling towers can reduce the cost of makeup water.

Discharge of Refinery Wastewater to Municipal Sewers

Available data indicates that only about 1-2 percent of the process wastewater from U. S. oil refineries is discharged to municipal sewers. The major reason is that almost all sewer regulations include a prohibition of discharge of oil and inflammable and explosive materials. Even the more permissive proposed regulations for discharge of essentially untreated industrial waste to municipal sewers require that no straight oils, tars, greases, petroleum products or concentrated emulsions enter the system. These materials are generally rejected because of problems both in the sewer and in the treatment plant. Oil materials tend to cling to the walls of the sewer, thus adversely effecting hydraulic properties and becoming a fire or explosive hazard. In the treatment plant, large amounts of oil in the primary settling tanks will overload the skimming facilities and tend to keep solids in suspension due to the formation of emulsions. Large amounts of oil entering activated sludge or trickling filter units can interfere with biological action and oxygen transfer. High concentration of sulfides and mercaptans can be toxic to biological treatment. Phenols also cause trouble by formation of undesirable chlorophenols in the subsequent disinfection by chlorine. Although these problems are serious, they are not insurmountable, and oil refinery waste and municipal sewage can be treated together if it is first realized that pretreatment of the refinery wastewater is necessary.

Cooling and condensing waters generally are not segregated from process waters and hence the wastewaters from both sources would be handled together. In those few instances where cooling and condensing waters are segregated, they are usually either discharged directly to a waterway or reused by recycling through cooling towers. There is no information available which indicates that refineries discharge segregated cooling or condensing waters directly to municipal sewers.

A philosophy of waste treatment which has been receiving increased attention is the conveyance of municipal wastes to industrial wastewater treatment plants, which may be serving either an individual plant or a group of industries. The municipal sewage often provides needed nutrient materials as well as economic and tax benefits. As far as refinery wastes are concerned, certain pretreatment would be required prior to entry into any treatment plant. These include floatable oil separation (API Separation) and at times spent caustic neutralization and sour water stripping.

By-Product Utilization

The concept of byproduct utilization as applied to petroleum refining is limited to those materials which, if recovered, would accrue some economic benefit but not necessarily enough to cover the cost of recovery.

Based on this definition, the major byproduct is sulfur, which is recovered from sour waters and from the hydro-treating process. In 1966, the value of sulfur recovered was estimated at $40,000,000. This value is likely to increase greatly in the near future, primarily because of the increased demand for low-sulfur fuels brought on by more stringent urban air pollution controls.

A number of other refining process wastes have been recovered or reused, although no meaningful cost data can be provided because of the highly volatile nature of the market for such products, variations in refinery accounting practices relative to credit for reused materials, and similar reasons. The recovered materials include:

1. Recovery of sulfuric acid from sludges produced in the acid treatment of oils. Hydrolysis of the sludge produces a dilute (30-60%) black acid of rather limited utility.

2. Reuse of spent alkylation acid in the treatment of oils and waxes, with subsequent regeneration in captive or outside acid plants.

3. Sale of high-phenol waste caustics from treatment of catalytically-cracked naphthas.

4. Use of sprung phenols as refinery fuels. These materials come from acid springing of spent caustics from cracked naphtha treatment.

5. Use of various waste acids in slop oil treatment.

6. Recovery of aluminum chloride from hydrocarbon sludges, for use as a coagulant.

7. Recovery of acid oils by reaction of waste caustics with acids.

8. Use of boiler feedwater treatment sludge in the neutralization of wastewater.

9. Reuse of treated wastewater to supplement normal refinery water supply.

10. Recovery of ammonia and hydrogen sulfide from sour water stripping for use as raw materials in the manufacture of fertilizer grade ammonium sulfate.

WASTE TREATMENT COSTS

1966 Replacement Value and Operating Costs

A comprehensive report on waste treatment costs in the petroleum refining industry in 1959 indicated that, on the basis of 183 refineries reporting (out of a possible 313), replacement and operating costs for waste treatment processes totalled $156,000,000 and $30,000,000 respectively. These costs were calculated by extrapalating to account for 100 percent of the crude capacity at that time. In 1959, planned additions to waste treatment facilities for 134 refineries totalled $29,000,000.

The data from this 1959 report were used as the basis for calculation of replacement value and operating costs for 1966. The factors used to update the data were assumption of a 30 percent increase in construction and operating costs, and extrapolation of the value of the 1959 planned additions for 134 refineries to cover the 1966 total of 279 refineries. In this manner the 1966 wastewater facilities replacement value was estimated to be $275,000,000 and the related annual operating costs $55,000,000.

Capital and Annual Costs of Various Treatment Processes

Wastewater flows and principal pollutant loadings for small, medium, and large refineries of older typical and newer technologies are summarized in Table 13. Capital and annual costs for the specific waste treatment processes required to handle these wastes adequately on an end-of-pipe basis are presented in Tables 14, 15, and 16. The capital costs are based on estimates of 1967 construction costs, including an allowance of 15 percent for contingencies; they do not include design or other engineering fees. The annual costs include operating labor, maintenance, utilities, and chemicals costs but no fixed charges for depreciation, interest, taxes, etc.

The end-of-pipe treatment costs of Tables 14, 15, and 16 were prorated among the individual fundamental processes. This allocation of treatment costs is considered the most reliable and most detailed breakdown that could be justified by available waste and processing data and by current and reasonably expected future industry practice. Costs based on separate waste treatment plants for specific processes or subprocesses would not be realistic, because there are compelling technical and economic reasons for combined treatment in most cases. Spent caustic, sour water, and at times separable oil are the only wastewater streams for which treatment on an individual process unit basis can be justified.

The first step in the cost allocation is prorating the wastewater flow and BOD loadings. Table 17 gives the percentages of overall refinery flow and BOD contributed by each of the major fundamental processes. These figures were calculated from the wastewater flows and loadings of Table 4, discussed earlier. Particular note should be made of the "unaccounted" entry at the bottom of the table, from which it is obvious that the BOD in the total wastewater of older and typical refineries cannot be adequately accounted for by a summation of the individual process effluents. This circumstance makes the allocation procedure less than completely satisfactory, but it also indicates that direct evaluation of waste treatment costs on a specific process basis (instead of end-of-pipe treatment) would be virtually impossible.

The desirable final step in cost allocation would be to spread the costs of each separate waste treatment process over each of the fundamental manufacturing process for small, medium, and large refineries in the older, typical, and newer technology categories; this would require more than 100 separate tables. To overcome this formidable obstacle and still obtain a reasonable estimate of waste treatment costs, three end-of-the-pipe wastewater treatment trains were developed to represent low, intermediate, and high degrees of treatment.

The composition of these treatment trains is as follows:

Low - API Separator and Slop Oil Treatment.

Intermediate - API Separator, Slop Oil Treatment, Aerated Lagoon, and Sour Water Stripping.

High - API Separator, Slop Oil Treatment, Sour Water Stripping, Activated Sludge Treatment, Sludge Thickening and Vacuum Filtration, and Sludge Incineration.

The flow and BOD allocations of Table 17 and the treatment process cost figures of Table 15 (for a typical refinery) were the principal bases for calculation of the treatment cost allocations presented in Table 18. The cost allocations for the treatment trains involving Slop Oil and Sour Water Treatment included consideration (see Table 19) of portions of these treatment processes attributed to the various fundamental processes.

The most significant feature of the final treatment cost allocations of Table 16 is that about 50 to 70 percent of the capital and annual costs is allocated to the crude oil fractionation and catalytic cracking processes.

Effect of In-Plant Waste Reduction Practices

Although detailed cost information is not available on cost justification of in-plant process modifications, an indication of the approximate cost savings is afforded by the estimated effect of a reduction in organic and hydraulic loading upon capital costs of wastewater treatment facilities for a 100,000 bpsd refinery, as presented in Figure 4. The high-degree waste treatment train upon which this analysis is based includes an API separator, activated sludge system (aeration basin and secondary clarification), and sludge thickening, vacuum filtration, and incineration.

Upon inspection of Figure 4 it can be seen that a 50 percent reduction in BOD (flow remaining constant) would result in a 15 percent reduction in costs. Similarly, a 50 percent reduction in flow (with BOD constant) would result in a 20 percent cost reduction. If both BOD and Flow are reduced by 50 percent, treatment costs would be reduced by 32 percent. An important factor in the relatively shallow rate of decrease is the insensitivity of incineration costs to waste load reduction in this size range. Incineration costs are relatively constant below five (5) tons/day; thus the reduction in BOD load in a 100,000 bpsd refinery has little effect on reducing incinerator costs.

APPENDIX A

Table 1

Estimated Percentage of Petroleum Refineries Using Various Fundamental Manufacturing Processes and Alternative Subprocesses

	1950	1963	1967	1972	1977	Technology
A. Crude Oil Desalting		100	100	100	100	
1. Chemical Desalting		5	2	0	0	0
2. Electrostatic Desalting		95	97	100	100	T,N
B. Crude Distillation	100	100	100	100	100	
1. Atmospheric Fractionator	100	100	100	100	100	0,T,N
2. Vacuum Fractionator		60	64	70	75	0,T,N
3. Vacuum Flasher						0,T,N
C. Thermal Cracking	59	48	45	40	35	
1. Thermal Cracking		28	18	8	2	0
2. Delayed Coking		12	14	16	19	T,N
3. Visbreaking		13	16	18	22	T,N
4. Fluid Coking		2	2	4	6	T,N
D. Catalytic Cracking	25	51	56	60	65	
1. Fluid Catalytic Cracking		39	45	50	60	T,N
2. Thermofor Catalytic Cracking		13	12	10	6	0
3. Houdriflow			3	2	0	0
E. Hydrocracking	0	2	8	25	34	
1. Isomax			4	11	15	N
2. Unicracking			2	8	12	N
3. H-G Hydrocracking		0.3	0.8	3	3	N
4. H-Oil			0.4	1	1	N
F. Reforming		62	67	74	79	
1. Platforming		37	40	44	47	0,T,N
2. Catalytic Reforming - Engelhard		5	9	11	12	0,T
3. Powerforming		1	2	3	3	T,N
4. Ultraforming		6	6	7	8	T,N

Table 1 (Cont.)

Estimated Percentage of Petroleum Refineries
Using Various Fundamental Manufacturing Processes
and Alternative Subprocesses

	1950	1963	1967	1972	1977	Technology
G. Polymerization	25	42	33	26	7	
1. Bulk Acid Polymerization						T,N
2. Solid Phosphoric Acid Condensation						T
3. Sulfuric Acid Polymerization						O
4. Thermal Polymerization		1	0.4			O
H. Alkylation	10	38	47	54	62	
1. Sulfuric Acid Alkylation		22	26	32	38	T,N
2. HF Alkylation		16	21	22	25	O,T,N
3. DIP Alkylation						N
4. Thermal Alkylation						O
I. Isomerization		5	7	10	15	
1. Isomerate		1	1.5	3	6	N
2. Liquid-Phase Isomerization		2	3	4	5	N
3. Butamer		1	1	2	2	N
4. Penex		0.7	1	1	2	N
J. Solvent Refining		25	29	30	32	
1. Furfural Refining		14	15	16	16	O,T,N
2. Duo-Sol		2	3	3	3	T,N
3. Phenol Extraction		10	10	11	11	O,T,N
4. Udex		3	5	8	8	T,N
K. Dewaxing		11	11	11	11	
1. Solvent Dewaxing(MEK)		8	8	9	9	O,T,N
2. Propane Dewaxing		2	2	2	2	O,T
3. Pressing and Sweating		1	1	0	0	O

Table 1 (Cont.)

Estimated Percentage of Petroleum Refineries
Using Various Fundamental Manufacturing Processes
and Alternative Subprocesses

	1950	1963	1967	1972	1977	Technology
L. Hydrotreating		47	56	70	80	
1. Unifining		22	23	30	35	T,N
2. Hydrofining		3	3	5	8	T,N
3. Trickle Hydrodesulfurization		0.3	2	4	5	T,N
4. Ultrafining		3	5	8	10	T,N
M. Deasphalting		20	23	25	27	
1. Propane Deasphalting and Fractionation		15	18	20	21	O,T,N
2. Solvent Decarbonizing		4	5	5	6	T,N
N. Drying and Sweetening		80	80	80	80	
1. Copper Sweetening						O,T
2. Doctor Sweetening						O
3. Merox						N
4. Girbotol						O,T,N
O. Wax Finishing		11	11	11	11	
1. Wax Fractionation		10	9	6	5	O,T
2. Wax Manufacturing, MIBX		1	1	1	1	O,T
3. Hydrotreating			1	4	5	N
P. Grease Manufacture		12	12	10	10	O,T,N
Q. Lube Oil Finishing		19	19	20	20	
1. Perculation Filtration		11	7	5	2	O,T
2. Continuous Contact Filtration		6	7	7	7	O,T
3. Hydrotreating		2	5	8	11	N
R. Hydrogen Manufacture		2	8	25	34	
1. Hydrogen Partial Oxidation		1	3	10	12	N
2. Hydrogen, Steam Reforming		1	5	15	22	N
Total No. of Refineries	346	293	261	236	211	

Table 2

Classification of U.S. Petroleum Refineries by Size and Degree of Technology

		Percent of Total		
	Small	Medium	Large	Total
Technology	Up to 35,000 bpsd	35-100,000 bpsd	>100,000 bpsd	
Older	31.2	4.4	0.4	36.0
Typical	32.5	17.4	7.0	56.9
Newer	3.4	1.3	2.4	7.1
Total (based on No. of Refineries)	67.1	23.1	9.8	100.0
Total (based on Crude Capacity	19.6	34.7	45.7	100.0

Table 3

Qualitative Evaluation of Wastewater Flow and Characteristics by Fundamental Refinery Processes

Fundamental Processes	Flow	BOD	COD	Phenol	Sulfide	Oil	Emulsified Oil	pH	Temp.	Ammonia	Chlorides	Acidity	Alkalinity	Susp. Solids
Crude Oil and Product Storage	XX	X	XXX	--	--	XXX	XX	0	0	0		0		XX
Crude Oil Desalting	XX	XX	XX	X	XXX	X	XXX	X	XXX	XX	XXX	0	X	XXX
Crude Oil Distillation	XXX	X	X	XX	XXX	XX	XXX	X	XX	XXX	X	0	X	X
Thermal Cracking	X	X	X	X	X	X	--	XX	XX	X	X	0	XX	X
Catalytic Cracking	XXX	XX	XX	XXX	XXX	X	X	XXX	XX	XXX	X	0	XXX	X
Hydrocracking	X	--	--	--	XX	--	--	--	XX	--	--	--	--	--
Reforming	X	0	0	X	X	X	0	0	X	X	0	0	0	0
Polymerization	X	X	X	0	X	X	0	X	X	X	X	X	0	X
Alkylation	XX	X	X	0	XX	X	0	XX	X	X	XX	XX	0	XX
Isomerization	X	--	--	--	--	--	--	--	--	--	--	--	--	--
Solvent Refining	X	--	X	X	0	--	X	X	0	--		0	X	
Dewaxing	X	XXX	XXX	X	0	X	0	--	--	--	--	--	--	--
Hydrotreating	X	X	X	--	XX		0	XX	--	0	0	0	X	0
Drying and Sweetening	XXX	XXX	X	XX	0	0	X	XX	0	X	0	X	X	XX

XXX - Major Contribution
XX - Moderate Contribution
X - Minor Contribution
0 - No Problem
-- - No Data

Table 4

Waste Loadings and Wastewater Volumes Associated with Fundamental Processes in Older, Typical, and Newer 100,000 bpsd Refineries

Fundamental Process	Older Technology					Typical Technology					Newer Technology				
	Process Capacity 1000 bpsd	Flow mgd	BOD lb/day	Phenol lb/day	Sulfides lb/day	Process Capacity 1000 bpsd	Flow mgd	BOD lb/day	Phenol lb/day	Sulfides lb/day	Process Capacity 1000 bpsd	Flow mgd	BOD lb/day	Phenol lb/day	Sulfides lb/day
Crude Oil Product Storage	100	0.04	100	*	*	100	0.04	100	*	*	100	0.04	100	*	*
Crude Desalting	100	0.02	200	20	200	100	0.02	200	10	200	100	0.02	200	5	200
Crude Fractionation	100	10.00	2000	300	100	100	5.00	20	100	100	100	1.00	20	100	100
Thermal Cracking	20	1.32	20	140	40	15	0.03	15	3	15	10	0.02	10	2	10
Catalytic Cracking	50	4.25	3100	2500	1500	50	1.50	500	1000	150	50	0.25	500	250	150
Hydrocracking		not in this technology					not in this technology				14	0.07	*	*	*
Reforming	15	0.14	t	10	t	20	0.12	t	14	20	23	0.14	t	16	23
Polymerization	1.3	0.39	4	2	286	1	0.14	3	t	10		not in this technology			
Alkylation	2	0.35	2	t	10	6	0.36	6	1	60	6	0.12	6	1	120
Isomerization		not in this technology					not in this technology				1	*	*	*	*
Solvent Refining	6	0.05	*	18	t	6	0.05	*	18	t	6	0.05	*	18	t
Dewaxing	4	0.99	2080	8	t	4	0.09	2000	6	t	4	0.08	1000	6	t
Hydrotreating	10	0.01	20	6	70	35	0.04	70	t	70	40	0.32	80	t	80
Deasphalting	3	*	*	*	*	3	*	*	*	*	3	*	*	*	*
Drying and Sweetening	50	5.00	5000	500	*	50	2.00	2500	500	*	45	1.80	2250	450	*
Wax Finishing	0.5	*	*	*	*	0.5	*	*	*	*	0.5	*	*	*	*
Grease Manufacture	0.2	*	*	*	*	0.2	*	*	*	*	0.2	*	*	*	*
Lube Oil Finishing	4	*	*	*	*	4	*	*	*	*	4	*	*	*	*
Hydrogen Manufacture	--	not in this technology				--	not in this technology				--	*	*	*	*
Blending and Packaging	100					100					100				
Summation		23.10	12,526	3,504	2,206		9.93	5,414	1,652	625		4.45	4,166	848	683
Unaccounted		(1.9)	(27,474)	--	--		(.07)	(4,586)	--	--		(.55)	(834)	--	--
Total Plant Effluent (after API Separator)		25.0	40,000	3,000	1,000		10.0	10,000	1,000	300		5.00	5,000	500	300

* data not available for reasonable estimate

t - trace

Table 5

Waste Loadings and Volumes Per Unit of Fundamental Process Throughput
In Older, Typical, and Newer Technologies

Fundamental Process	Older Technology				Typical Technology				Newer Technology			
	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl	Flow gal/bbl	BOD lbs/bbl	Phenol lbs/bbl	Sulfides lbs/bbl
Crude Oil and Product Storage	4	0.001	*	*	4	0.001	*	*	4	0.001	*	*
Crude Desalting	[illegible]	0.002	0.20	0.002	2	0.002	0.10	0.002	2	0.002	0.05	0.002
Crude Fractionation	100	0.020	3.0	0.001	50	0.0002	1.0	0.001	10	0.0002	1.0	0.001
Thermal Cracking	66	0.001	7.0	0.002	2	0.001	0.2	0.001	1.5	0.001	0.2	0.001
Catalytic Cracking	85	0.062	50.0	0.03	30	0.010	20	0.003	5	0.010	5	0.003
Hydrocracking		not in this technology				not in this technology			5	*	*	*
Reforming	9	t	0.7	t	6	t	0.7	0.001	6	t	0.7	0.001
Polymerization	300	0.003	1.4	0.22	140	0.003	0.4	0.010		not in this technology		
Alkylation	173	0.001	0.1	0.005	60	0.001	0.1	0.010	20	0.001	0.1	0.020
Isomerization		not in this technology				not in this technology			*	*	*	*
Solvent Refining	8	*	3	t	8	*	3	t	8	*	3	t
Dewaxing	247	0.52	2	t	23	0.50	1.5	t	20	0.25	1.5	t
Hydrotreating	1	0.002	0.6	0.007	1	0.002	0.01	0.002	8	0.002	0.01	0.002
Deasphalting	*	*	*	*	*	*	*	*	*	*	*	*
Drying and Sweetening	100	0.10	10	*	40	0.05	10	*	40	0.05	10	*
Wax Finishing	*	*	*	*	*	*	*	*	*	*	*	*
Grease Manufacture	*	*	*	*	*	*	*	*	*	*	*	*
Lube Oil Finishing	*	*	*	*	*	*	*	*	*	*	*	*
Hydrogen Manufacture		not in this technology				not in this technology			*	*	*	*
Blending and Packaging	*	*	*	*	*	*	*	*	*	*	*	*

* Data not available for reasonable estimate.
t - Trace.

Table 6

Summary of Principal Waste Loads and Wastewater Volumes

Total Refinery Effluent after API Separator per Barrel of Crude Oil Throughput

Type of Technology	Flow gal/bbl		BOD lbs/bbl		Phenol lbs/bbl		Sulfide lbs/bbl	
	avg.	range	avg.	range	avg.	range	avg.	range
Older	250	170-374	.40	.31-.45	.030	.028-.033	.01	.008-.013
Typical	100	80-155	.10	.08-.16	.01	.009-.013	.003	.0028-.008
Newer	50	20-60	.05	.02-.06	.005	.001-.006	.003	.0015-.003

Waste Loads from 100,000 bpsd Refinery Based on Total Refinery Effluent after API Separator

Type of Technology	Flow mgd	BOD lbs/day	Phenol lbs/day	Sulfide lbs/day
Older	25.0	40,000	3,000	1,000
Typical	10.0	10,000	1,000	300
Newer	5.0	5,000	500	300

Waste Loads from 100,000 bpsd Refinery Based on Specific Process Unit Waste Loads[1]

Type of Technology	Flow mgd	BOD lbs/day	Phenol lbs/day	Sulfide lbs/day
Older	23.10	12,526	3,504	2,206
Typical	9.93	5,414	1,652	625
Newer	4.45	4,166	848	683

[1] Summarized from Table 4

Table 7

Estimated Wastewater Flows and Waste Loads

per Unit of Various Refinery Products

Product	Older Technology				Typical Technology				Newer Technology			
	Flow Gal/bbl	BOD lbs/1000 bbl	Phenol lbs/1000 bbl	Sulfide lbs/1000 bbl	Flow Gal/bbl	BOD lbs/1000 bbl	Phenol lbs/1000 bbl	Sulfide lbs/1000 bbl	Flow Gal/bbl	BOD lbs/1000 bbl	Phenol lbs/1000 bbl	Sulfide lbs/1000 bbl
LPG	423	229	137	89	163	44	56	13	49	52	18	13
Benzene	175	73	9.0	3.7	93	29	8.1	3.9	56	26	9	6.1
Aromatics	153	94	8.6	3.4	84	17	7.1	5.6	47	16	6.8	6.0
Gasoline	225	110	38	27	103	35	18	6.8	44	33	8.8	7.5
Naphtha	208	99	14	5.2	87	42	19	5.2	47	39	7.8	4.8
Jet Fuel	181	92	18	8.9	85	35	10	8.9	41	33	7.1	3.6
Kerosine	156	73	8.2	3.7	76	29	6.1	3.7	35	26	5.6	3.8
Alkylate	335	161	62	36	177	53	29	35	71	49	13	28
Furnace Oil	144	112	39	21	95	44	17	5.7	42	34	8.7	5.7
Lubricating Oil	322	398	12	3.9	100	335	10	5.2	60	185	9.4	4.0
Greases	[illegible]	1163	22	4.4	150	1055	18	4.5	110	549	17	4.5
Wax	790	1331	25	3.8	164	1234	22	3.8	120	631	21	4
Asphalt	106	23	3.2	3.0	56	3.2	1.1	3	16	3	1.0	3.0
Coke	190	24	12	5.6	58	4.2	1.4	4.2	17	4	1.2	3.6

Note:

Some fundamental processes missing (hydrocracking, isomerization, deasphalting, wax finishing, hydrogen manufacture, blending and packaging).

Table 8

Projections of Total U. S. Petroleum Refinery Gross Waste Loads and Wastewater Volumes to 1977

Year	Flow gal/day	BOD lbs/day	Phenol lbs/day	Sulfide lbs/day
1963	1.04×10^9	1.04×10^6	1.04×10^5	3.14×10^4
1968	1.09×10^9	1.23×10^6	1.23×10^5	3.70×10^4
1969	1.10×10^9	1.26×10^6	1.26×10^5	3.82×10^4
1970	1.11×10^9	1.30×10^6	1.30×10^5	3.93×10^4
1971	1.12×10^9	1.34×10^6	1.34×10^5	4.04×10^4
1972	1.13×10^9	1.38×10^6	1.38×10^5	4.15×10^4
1977	1.18×10^9	1.56×10^6	1.56×10^5	4.71×10^4

Table 9

Monthly Variation of Total Crude Throughput and Gasoline and Distillate Fuel Oil Production[1]

(in thousands of barrels)

1964	Total Crude Throughput	Gasoline	Distillate Fuel Oil
January	275,585	140,586	67,443
February	257,221	131,404	62,812
March	268,473	138,527	61,681
April	255,555	132,911	57,525
May	268,273	138,996	60,775
June	270,258	138,975	61,092
July	285,774	147,552	64,184
August	282,273	147,610	61,986
September	268,107	140,521	59,347
October	274,601	144,924	59,552
November	263,295	139,654	58,881
December	281,236	145,785	66,768
1965			
January	282,328	147,894	66,765
February	256,222	132,772	60,930
March	274,888	142,029	62,188
April	161,080	135,685	58,544
May	274,493	140,097	61,453
June	273,932	144,214	58,692
July	292,054	150,981	65,497
August	291,946	152,775	66,370
September	274,390	142,908	62,744
October	280,540	144,897	65,652
November	278,608	144,977	66,112
December	292,472	154,029	70,124

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[1] Annual Statistical Bulletin, Department of Statistics American Petroleum Institute, April, 1966.

Table 10

Efficiency Of Oil Refinery Waste Treatment Practices
Based On Effluent Quality

	MPPI*	BOD	COD	Separable Oil	Emulsified Oil	Phenol	Sulfide S	Susp. Solids	Chloride	Ammonia	Acidity Alkalin.	Cyanide	pH	Toxicity	Temp.
PHYSICAL TREATMENT															
API Separators	R.W.	5-35[1]	5-30[1]	60-99	N.A.	Reduced	N.A.	10-50	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Earthen Separators	R.W.	5-50	5-40	50-99	N.A.	Reduced	N.A.	10-85	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	10-90[2]
Evaporation	API Eff.	100	100	N.A.	100	100	100	100	100	100	100	100	N.A.	N.A.	N.A.
Air Flotation without chemicals	API Eff.	5-25	5-20	70-95	10-40	N.A.	Reduced	10-40	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
CHEMICAL TREATMENT															
Air Flotation with chemicals	API Eff.	10-60	10-50	75-95	50-90	N.A.	Reduced	50-90	N.A.	Reduced	N.A.	N.A.	N.A.	N.A.	N.A.
Chemical Coag. and Precip.	API Eff.	10-70	10-50	60-95	50-90	N.A.	N.A.	50-90	N.A.	N.A.	Altered	N.A.	Altered	N.A.	N.A.
BIOLOGICAL TREATMENT															
Activated Sludge	API Eff.	70-95	30-70	N.A.	50-80	65-99	90-99	60-85	N.A.	50-95	Altered	65-99	Altered	Reduced	10-60
Aerated Lagoons	API Eff.	50-90	25-60	N.A.	50-80	65-99	90-99	0-40	N.A.	0-45	Altered	65-99	Altered	Reduced	10-90
Trickling Filters	API Eff.	50-90	25-60	N.A.	50-80	65-99	80-99	60-85	N.A.	50-95	Altered	65-99	Altered	Reduced	10-60
Oxidation Ponds	API Eff.	40-80	20-50	N.A.	40-70	65-99	70-90	20-70	N.A.	20-90	Altered	65-99	Altered	Reduced	10-90
TERTIARY TREATMENT															
Activated Carbon	SEC.[4] Eff.	50-90	50-90	N.A.	50-90	80-99	80-99	N.A.	N.A.	10-30	N.A.	80-99	N.A.	Reduced	N.A.
Ozonation	SEC. Eff.	50-90	50-90	N.A.		80-99	80-99	N.A.	N.A.	10-30	N.A.	80-99	N.A.	Reduced	N.A.

[1] BOD and COD from separable oil not included.

[2] Percent of difference between ambient temperature and waste temperature.

[3] Limited by meteorological conditions.

[4] Chemical or Biological Treatment.

* MPPI Most Probable Process Influent indicates the kind and/or extent of prior treatment required for efficient utilization of the specific process under consideration.

Table 11

Degree of Adoption of Various Wastewater Treatment Processes

Processes and Subprocesses	Estimated Percentage of Refineries Employing Process 1950	1963	1967	1972	1977
API Separators	40	50	60	70	80
Earthen Basin Separators	60	50	40	30	20
Evaporation	0-1	0-1	1	1-2	2-5
Air Flotation	0-1	10	15	18	20
Neutralization (Total Wastewater)	0-1	0-1	0-1	0-1	0-1
Chemical Coagulation and Precipitation	1-5	1-5	5-10	10-15	10-15
Activated Sludge	0	5	10	40	55
Aerated Lagoons	0	5	10	25	30
Trickling Filters	1-2	7	10	10	10
Oxidation Ponds	10	25	25	25	20
Activated Carbon	0	0.5	0.5	3	5
Ozonation	0	1	1	3	5
Ballast Water Treatment-Phys.	9	9	8	5	5
Ballast Water Treatment-Chem.	1	1	2	5	5
Slop Oil-Vacuum Filtration	0	5	7	12	15
Slop Oil-Centrifugation	0	2	3	10	15
Slop Oil-Separation	100	93	90	80	70

Table 11

Degree of Adoption of Various Wastewater Treatment Processes

	Estimated Percentage of Refineries Employing Process				
Processes and Subprocesses	1950	1963	1967	1972	1977
API Separators	40	50	60	70	80
Earthen Basin Separators	60	50	40	30	20
Evaporation	0-1	0-1	1	1-2	2-5
Air Flotation	0-1	10	15	18	20
Neutralization (Total Wastewater)	0-1	0-1	0-1	0-1	0-1
Chemical Coagulation and Precipitation	1-5	1-5	5-10	10-15	10-15
Activated Sludge	0	5	10	40	55
Aerated Lagoons	0	5	10	25	30
Trickling Filters	1-2	7	10	10	10
Oxidation Ponds	10	25	25	25	20
Activated Carbon	0	0.5	0.5	3	5
Ozonation	0	1	1	3	5
Ballast Water Treatment-Phys.	9	9	8	5	5
Ballast Water Treatment-Chem.	1	1	2	5	5
Slop Oil-Vacuum Filtration	0	5	7	12	15
Slop Oil-Centrifugation	0	2	3	10	15
Slop Oil-Separation	100	93	90	80	70

Table 11 (cont'd.)

Degree of Adoption of Various Wastewater Treatment Processes

Processes and Subprocesses	Estimated Percentage of Refineries Employing Process 1950	1963	1967	1972	1977
Sour Water-Steam Stripping) -Flue Gas Strippers) -Natural Gas)	60	70	85	90	90
Sour Water-Air Oxidation	0	3	3-5	7	10
Sour Water-Vaporization	1	1-2	1	0	0
Sour Water-Incineration[1]	35-40	40	50	30	20
Neutralization of Spent Caustics					
Flue Gas	20	30	35	20	20
Spent Acid (including springing and stripping)	15	25	30	25	20
Oxidation	0	3	5	5	5
Incineration	25	40	50	20	15

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[1] Incineration includes flaring, boiler furnaces, and separate incinerators used only in conjunction with stripping and vaporization.

Table 12

Sequence/Substitution Diagram
Of Waste Treatment Processes

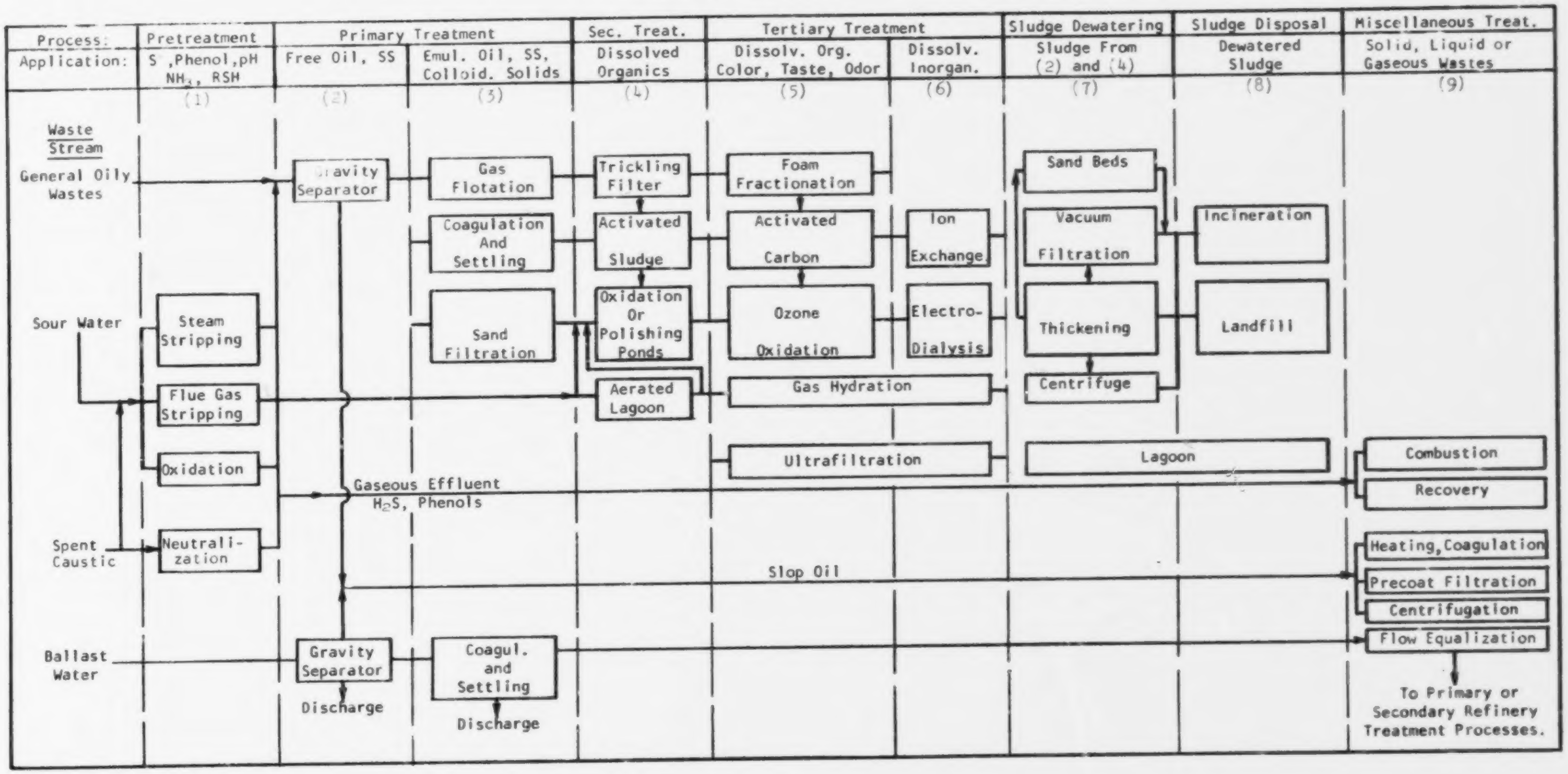

Process:
Application:
Pretreatment
S, Phenol, pH NH₃, RSH
(1)
Primary Treatment
Free Oil, SS
(2)
Emul. Oil, SS, Colloid. Solids
(3)
Sec. Treat.
Dissolved Organics
(4)
Tertiary Treatment
Dissolv. Org. Color, Taste, Odor
(5)
Dissolv. Inorgan.
(6)
Sludge Dewatering
Sludge From (2) and (4)
(7)
Sludge Disposal
Dewatered Sludge
(8)
Miscellaneous Treat.
Solid, Liquid or Gaseous Wastes
(9)
Waste Stream
General Oily Wastes
Sour Water
Spent Caustic
Ballast Water
Steam Stripping
Flue Gas Stripping
Oxidation
Neutralization
Gravity Separator
Gas Flotation
Coagulation And Settling
Sand Filtration
Trickling Filter
Activated Sludge
Oxidation Or Polishing Ponds
Aerated Lagoon
Foam Fractionation
Activated Carbon
Ozone Oxidation
Gas Hydration
Ultrafiltration
Ion Exchange
Electro-Dialysis
Sand Beds
Vacuum Filtration
Thickening
Centrifuge
Lagoon
Incineration
Landfill
Combustion
Recovery
Heating, Coagulation
Precoat Filtration
Centrifugation
Flow Equalization
Gaseous Effluent H₂S, Phenols
Slop Oil
Gravity Separator
Discharge
Coagul. and Settling
Discharge
To Primary or Secondary Refinery Treatment Processes.

Table 13

Pollutional Loads from Refineries of Various Technologies and Sizes

Technology	Size	Throughput (bpsd)	Flow (mgd)	BOD (lbs/day)	Phenol (lbs/day)	Sulfide (lbs/day)
Older						
	Small	30,000	7.5	12,000	900	300
	Medium	75,000	18.7	30,000	2,250	750
	Large	150,000	37.5	60,000	4,500	1,500
Typical						
	Small	30,000	3.0	3,000	300	90
	Medium	75,000	7.5	7,500	750	225
	Large	150,000	15.0	15,000	1,500	450
Newer						
	Small	30,000	1.5	1,500	300	90
	Medium	75,000	3.8	3,250	750	225
	Large	150,000	7.5	7,500	1,500	450

Table 14

Waste Treatment or Removal Cost Information*
Older Technology

Waste Treatment Process	Economic Life Years	Small Refinery		Medium Refinery		Large Refinery	
		Capital Costs Dollars	Annual Operating & Maintenance Costs Dollars	Capital Costs Dollars	Annual Operating & Maintenance Costs Dollars	Capital Costs Dollars	Annual Operating & Maintenance Costs Dollars
API Separator (Flow)	30	105,000	23,000	261,800	36,000	525,000	55,000
Earthen Separators with Skimming	100	9,500	17,500	23,500	24,250	47,000	27,000
Air Flotation (Flow)	20	222,750	37,000	553,250	74,000	995,000	117,750
Activated Sludge	30	655,000	120,000	1,425,000	187,000	2,850,000	375,000
Aerated Lagoon	30	110,000	24,500	240,000	51,500	480,000	103,000
Trickling Filters BOD	30	1,512,000	80,000	3,300,000	163,750	6,600,000	328,250
Oxidation Pond	100	120,000	4,000	252,000	4,000	528,000	7,500
Evaporation Pond (without dredging)	20	90,000	900	150,000	1,500	281,250	2,800
Thickening and Vacuum Filtration (Sludge)	20	120,500	22,000	150,000	50,000	265,000	58,750
Incineration (Sludge)	30	168,000	43,000	375,000	74,200	735,000	116,000
Slop Oil Treatment	50	114,000	11,000	281,500		563,000	
Sour Water Stripping	20	154,000		325,000		655,000	

*End-of-pipe Treatment

Table 15

Waste Reduction or Removal Cost Information*
Typical Technology

Waste Treatment Process	Economic Life Years	Small Refinery Capital Costs Dollars	Small Refinery Annual Operating & Maintenance Costs Dollars	Medium Refinery Capital Costs Dollars	Medium Refinery Annual Operating & Maintenance Costs Dollars	Large Refinery Capital Costs Dollars	Large Refinery Annual Operating & Maintenance Costs Dollars
API Separator	30	46,500	12,500	105,000	22,000	210,000	33,000
Earthen Separators with Skimming	100	4,000	11,000	9,500	17,500	19,000	24,000
Air Flotation	20	111,500	18,500	222,750	37,000	371,250	55,500
Activated Sludge (95% overall)	30	235,250	91,500	472.150	98,000	767,000	150,000
Aerated Lagoon 80%	30	36,000	18,750	72,000	24,500	132,000	41,250
Trickling Filters 80%	30	450,000	80,000	1,020,000	84,000	1,800,000	160,000
Oxidation Pond 80%	100	38,500	4,000	81,000	4,000	141,000	7,500
Evaporation Pond	20	56,250	575	90,000	900	127,500	1,275
Thickening and Vacuum Filtration (Sludge)	20	59,000	11,500	82,500	20,500	108,500	22,500
Incineration (Sludge)	30	187,000	19,000	198,000	32,200	202,000	49,000
Slop Oil Treatment	50	146,000		114,000	11,000	227,000	
Sour Water Stripping	20	63,000		154,000	15,000	263,000	

*End-of-pipe Treatment

Table 16

Waste Reduction or Removal Cost Information*

Newer Technology

Waste Treatment Process	Economic Life Years	Small Refinery Capital Costs Dollars	Small Refinery Annual Operating & Maintenance Costs Dollars	Medium Refinery Capital Costs Dollars	Medium Refinery Annual Operating & Maintenance Costs Dollars	Large Refinery Capital Costs Dollars	Large Refinery Annual Operating & Maintenance Costs Dollars
API Separator	30	30,000	11,000	53,200	13,000	105,000	23,000
Earthen Separators with Skimming	100	3,750	11,000	5,000	11,500	9,500	17,500
Air Flotation	20	70,000	14,500	181,500	25,500	222,750	37,000
Activated Sludge	30	125,750	67,000	251,000	91,000	472,000	98,000
Aerated Lagoon	30	20,000	15,000	36,500	20,000	72,000	24,500
Trickling Filters	30	255,000	56,250	487,500	80,000	1,020,000	85,000
Oxidation Pond	100	20,000	3,000	40,300	4,000	82,500	4,000
Evaporation Pond	20	40,000	500	66,500	700	90,000	900
Thickening and Vacuum Filtration (Sludge)	20	35,000	9,500	62,500	12,000	82,500	20,500
Incineration (Sludge)	30	121,000	14,400	195,600	19,700	195,000	32,000
Slop Oil Treatment	50	22,500		57,000		114,000	
Sour Water Stripping	20	39,500		80,000		154,000	

*End-of-pipe Treatment

Table 17

Percent of Wastewater Flow and BOD Loading from Fundamental Refinery Processes

	Older		Typical		Newer	
Fundamental Process	Flow	BOD	Flow	BOD	Flow	BOD
Crude Oil Storage	1.6	0.25	4.0	1.0	8.0	2.0
Crude Oil Desalting	0.8	0.50	2.0	2.0	4.0	4.0
Crude Oil Fractionation	40.0	5.0	50.0	0.2	20.0	0.4
Thermal Cracking	5.3	0.05	0.3	0.15	0.4	0.2
Catalytic Cracking	17.0	7.75	15.0	5.0	5.0	10.0
Hydrocracking	-	-	-	-	1.4	-
Reforming	0.6	nil	1.2	nil	2.8	nil
Polymerization	1.6	0.01	1.4	0.03	-	-
Alkylation	1.4	0.005	3.6	0.06	2.4	0.12
Solvent Refining	0.2	-	0.5	-	1.0	-
Dewaxing	3.6	5.20	0.9	20.0	1.6	20.0
Hydrotreating	0.004	0.05	0.4	0.7	6.4	1.6
Drying and Sweetening	20.0	12.50	20.0	25.0	36.0	45.0
Sub Total	92.1	31.31	99.3	54.14	89.0	83.5
Unaccounted	7.9	68.7	0.7	44.9	11.0	16.5

Table 18

Treatment Cost Allocations to Fundamental Refinery Processes[1]

	Degree of Treatment					
	% of Total Cost					
	Low[2]		Intermediate[3]		High[4]	
Fundamental Process	Capital	Annual	Capital	Annual	Capital	Annual
Crude Oil Storage	1.9	2.7	1.6	2.5	2.4	2.7
Crude Oil Desalting	7.0	4.6	3.4	2.8	2.5	2.3
Crude Oil Fractionation	50.1	50.0	41.2	45.0	34.2	35.4
Thermal Cracking	5.3	3.5	6.2	3.8	2.6	1.6
Catalytic Cracking	17.6	16.6	19.7	17.8	14.4	13.5
Hydrocracking	2.6	1.7	4.7	2.8	1.9	1.0
Reforming	0.6	0.8	0.5	0.8	0.6	0.6
Polymerization	0.7	0.9	0.6	0.9	0.7	0.9
Alkylation	1.7	2.4	1.5	2.3	1.8	2.2
Solvent Refining	0.4	0.4	0.2	0.3	0.3	0.3
Dewaxing	0.4	0.6	0.4	0.6	5.5	5.7
Hydrotreating	0.2	0.3	5.4	3.3	2.5	1.6
Drying and Sweetening	9.6	13.3	11.4	14.9	17.9	19.6
Unaccounted	1.9	2.2	3.2	2.2	12.7	12.6
Total (%)	100.0	100.0	100.0	100.0	100.0	100.0
Total (Dollars)	219,000	33,000	445,000	72,500	1,126,000	187,000

---

[1] Typical 100,000 bpsd refinery.

[2] API Sep., Slop Oil Treatment.

[3] API Sep., Aer. Lagoon, Slop Oil Treatment, Sour Water Strip.

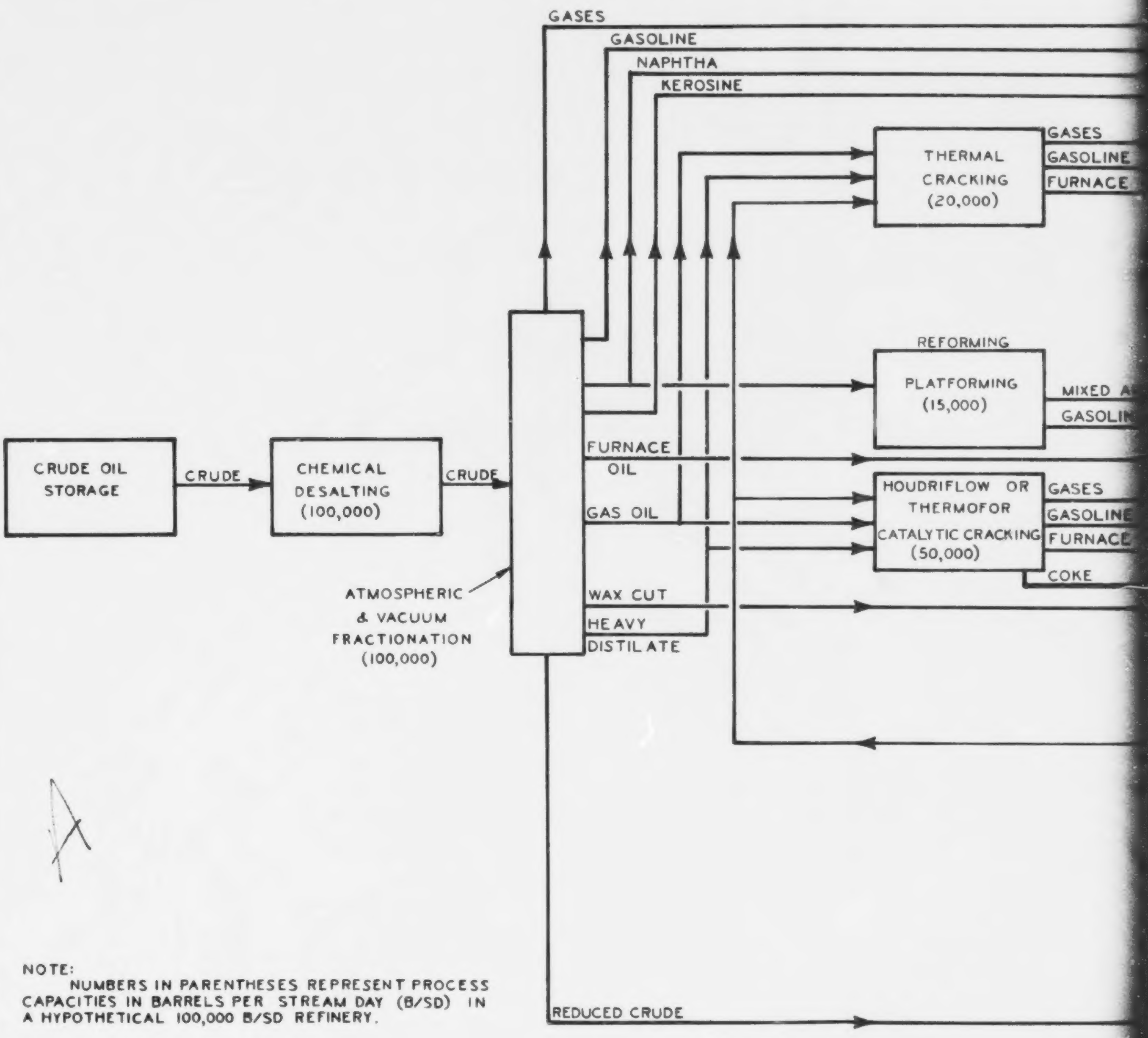
[4] API Sep., Act. Sludge, Thick., Vac. Filt., Incin., Slop Oil Treatment, Sour Water Strip.

Table 19

Estimated Percent of Sour Waters and Slop Oil from Fundamental Processes of Typical 100,000 bpsd Refinery

Fundamental Process	Sour Waters	Slop Oil
Crude Oil Storage	Negligible	Negligible
Crude Oil Desalting	Negligible	10
Crude Oil Fractionation	25	50
Thermal Cracking	10	10
Catalytic Cracking	25	20
Hydrocracking	10	5
Reforming	5	5
Polymerization		
Alkylation		
Solvent Refining		
Dewaxing		
Hydrotreating	15	
Drying and Sweetening	10	

APPENDIX B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NAPHTHA
KEROSINE
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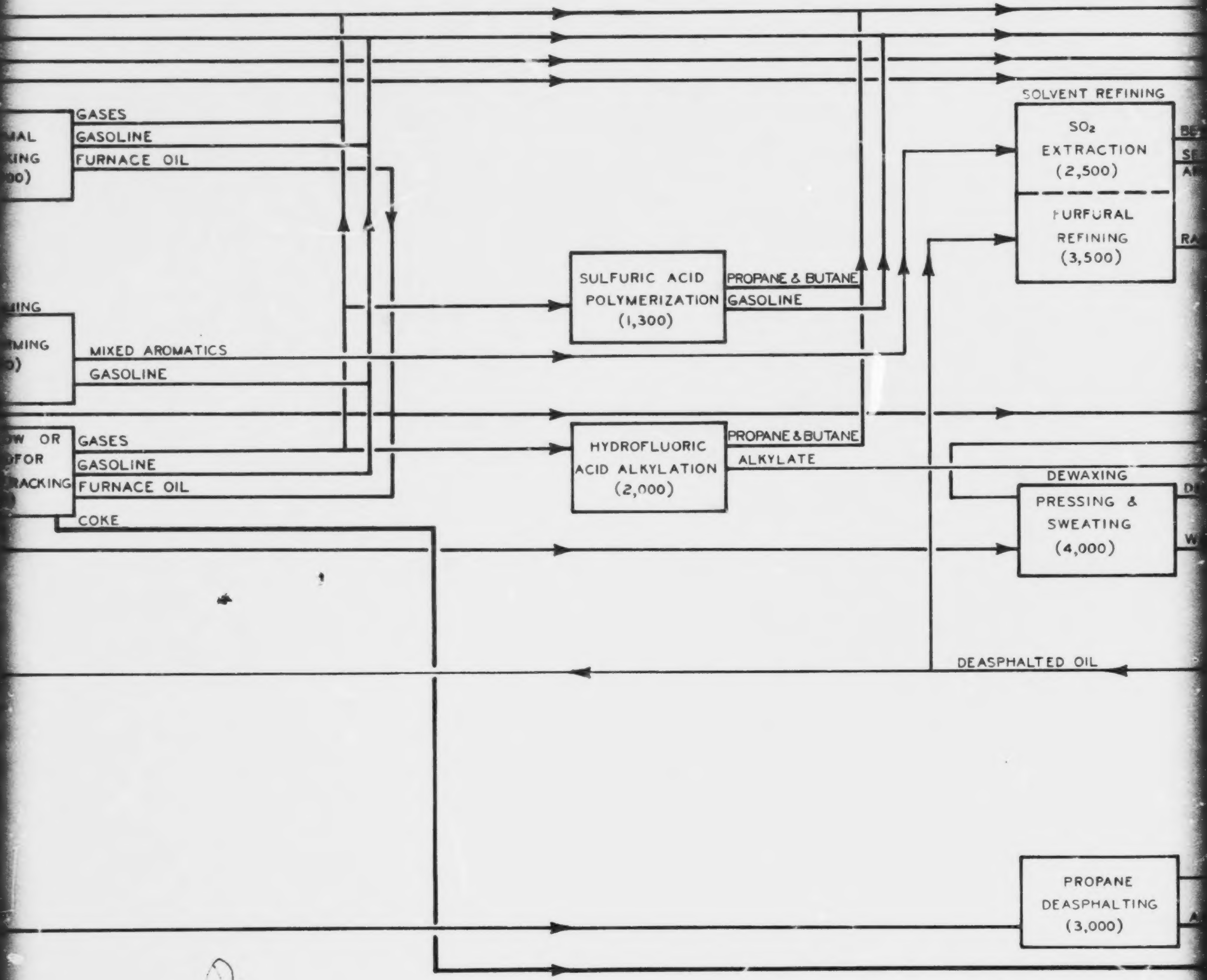
GASES
GASOLINE
FURNACE
REFORMING
PLATFORMING (15,000)
MIXED A
GASOLIN
CRUDE OIL STORAGE
CRUDE
CHEMICAL DESALTING (100,000)
CRUDE
FURNACE OIL
GAS OIL
HOUDRIFLOW OR THERMOFOR CATALYTIC CRACKING (50,000)
GASES
GASOLINE
FURNACE
COKE
ATMOSPHERIC & VACUUM FRACTIONATION (100,000)
WAX CUT
HEAVY DISTILATE
REDUCED CRUDE

NOTE:
NUMBERS IN PARENTHESES REPRESENT PROCESS CAPACITIES IN BARRELS PER STREAM DAY (B/SD) IN A HYPOTHETICAL 100,000 B/SD REFINERY.

W. O. 30002

287-028 O - 68 (Face Reverse Of Appendix B) No. 1

SUBPROCESS SERIES REPRESENTATIVE OF AN OLDER TE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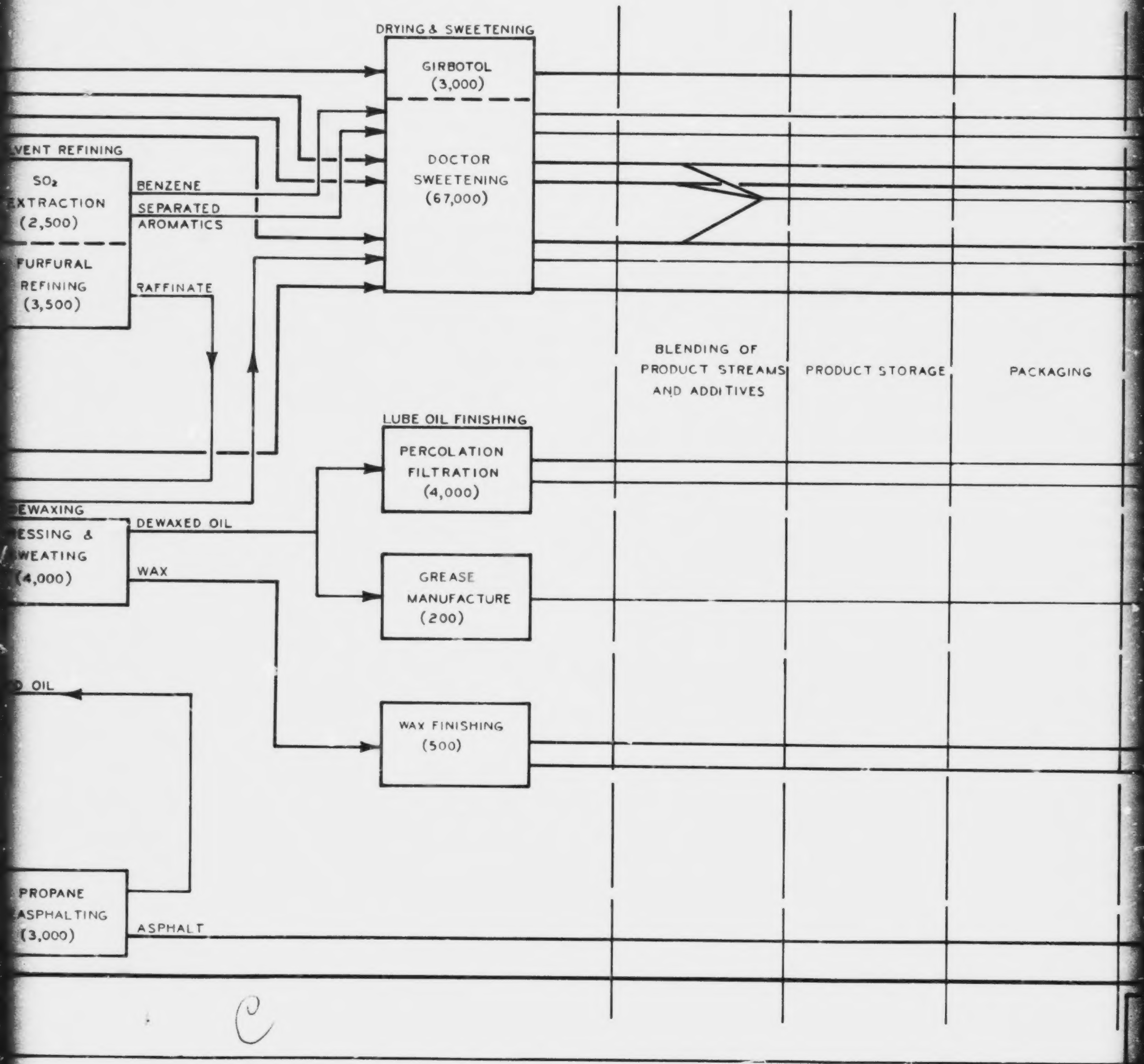
PROPANE & BUTANE
GASOLINE
MIXED AROMATICS
GASOLINE
GASES
GASOLINE
FURNACE OIL
COKE
HYDROFLUORIC ACID ALKYLATION (2,000)
PROPANE & BUTANE
ALKYLATE
SOLVENT REFINING
SO₂ EXTRACTION (2,500)
FURFURAL REFINING (3,500)
DEWAXING
PRESSING & SWEATING (4,000)
DEASPHALTED OIL
PROPANE DEASPHALTING (3,000)

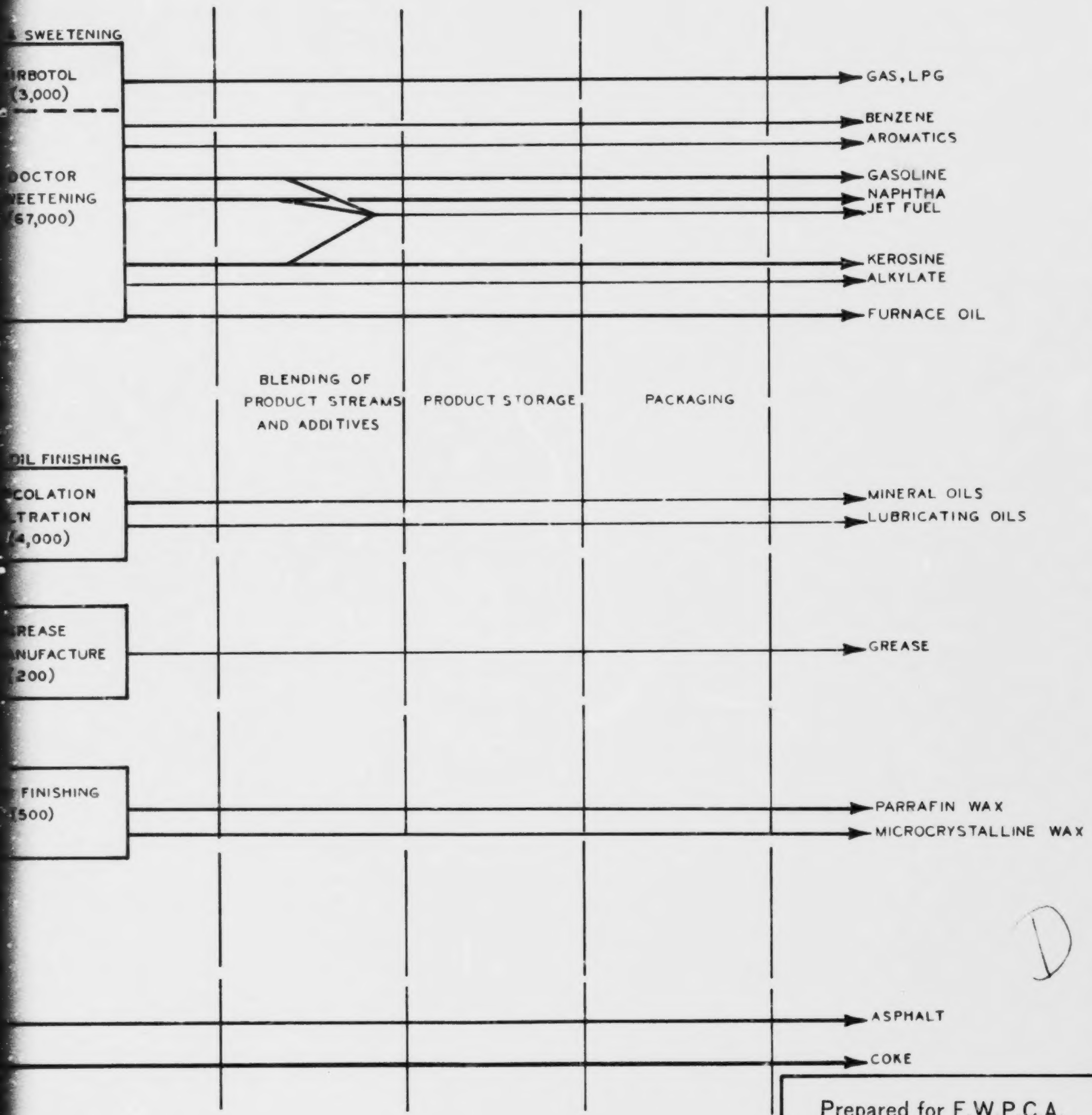
B

OLDER TECHNOLOGY



DRYING & SWEETENING
GIRBOTOL
(3,000)
DOCTOR
SWEETENING
(67,000)
VENT REFINING
SO₂
EXTRACTION
(2,500)
FURFURAL
REFINING
(3,500)
BENZENE
SEPARATED
AROMATICS
RAFFINATE
BLENDING OF
PRODUCT STREAMS
AND ADDITIVES
PRODUCT STORAGE
PACKAGING
LUBE OIL FINISHING
PERCOLATION
FILTRATION
(4,000)
DEWAXING
ESSING &
WEATING
(4,000)
DEWAXED OIL
WAX
GREASE
MANUFACTURE
(200)
OIL
WAX FINISHING
(500)
PROPANE
ASPHALTING
(3,000)
ASPHALT

C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IRBOTOL
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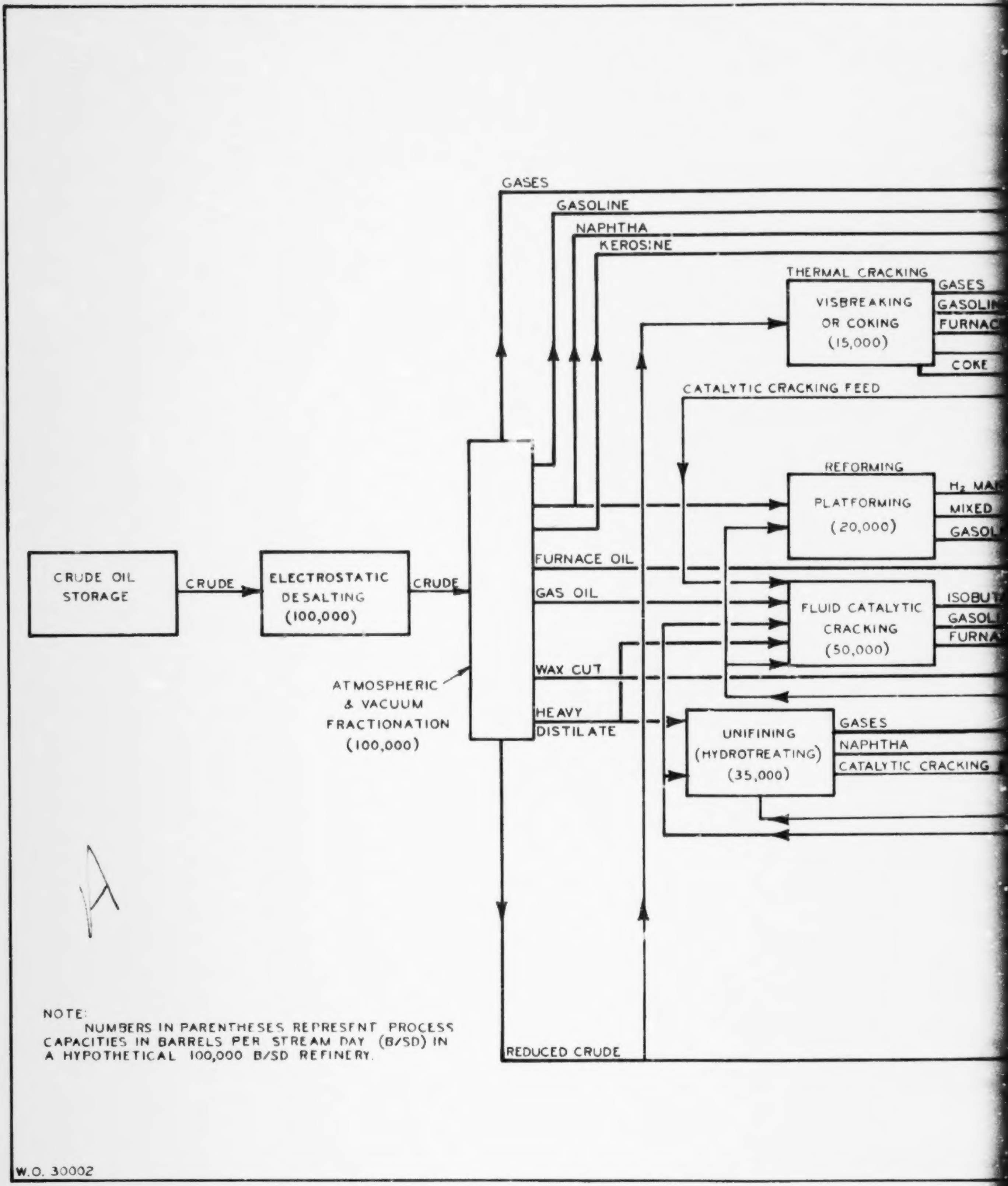
DOCTOR
WEETENING
(67,000)
GAS, LPG
BENZENE
AROMATICS
GASOLINE
NAPHTHA
JET FUEL
KEROSINE
ALKYLATE
FURNACE OIL
BLENDING OF PRODUCT STREAMS AND ADDITIVES
PRODUCT STORAGE
PACKAGING
OIL FINISHING
COLATION
LTRATION
(4,000)
MINERAL OILS
LUBRICATING OILS
REASE
NUFACTURE
(200)
GREASE
FINISHING
(500)
PARRAFIN WAX
MICROCRYSTALLINE WAX
ASPHALT
COKE

D

Prepared for F.W.P.C.A.

FIGURE 1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NAPHTHA
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GASES
GASOLIN
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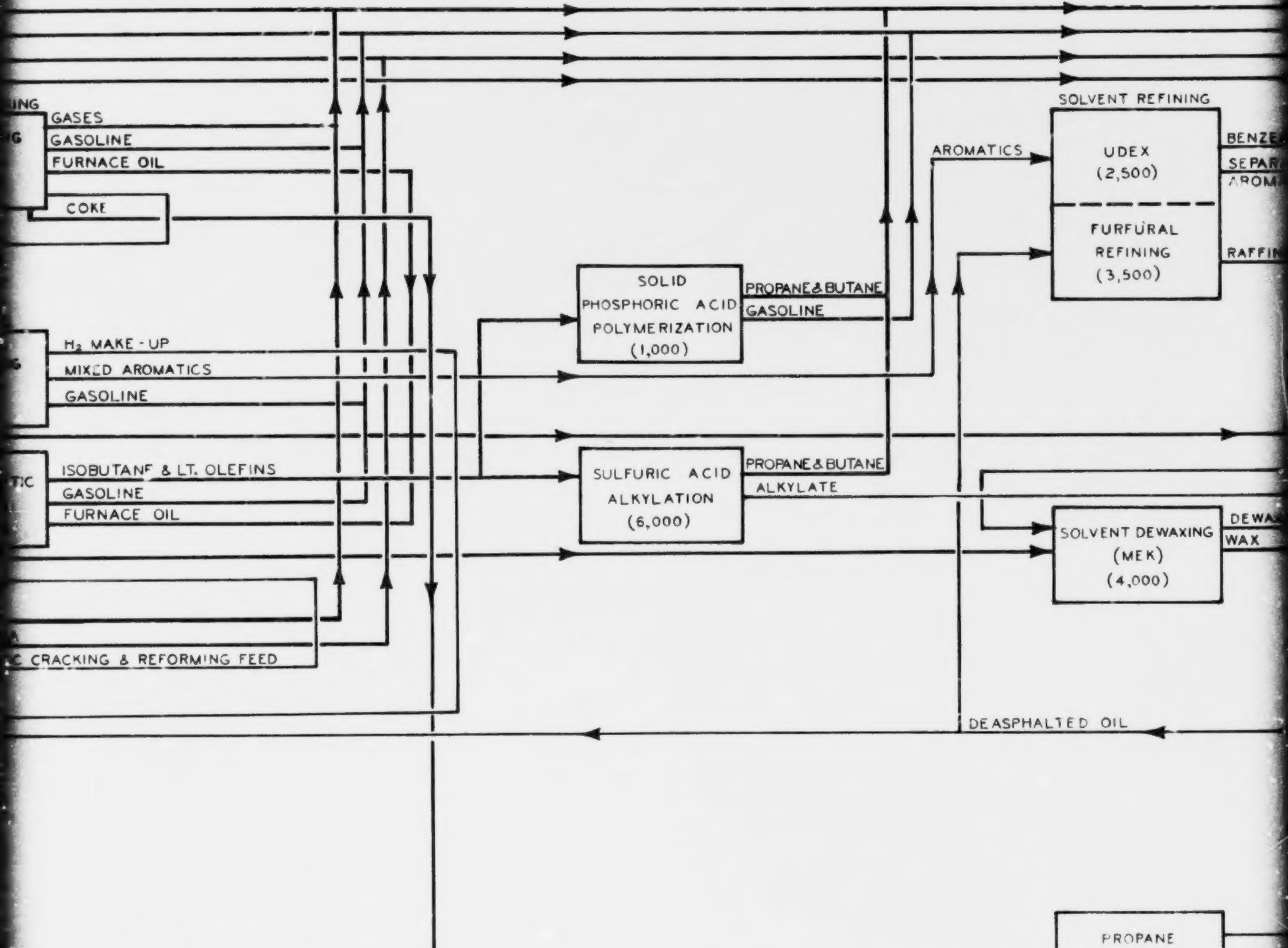
COKE
CATALYTIC CRACKING FEED
REFORMING
PLATFORMING (20,000)
H_2 MA
MIXED
GASOLI
CRUDE OIL STORAGE
CRUDE
ELECTROSTATIC DESALTING (100,000)
CRUDE
FURNACE OIL
GAS OIL
FLUID CATALYTIC CRACKING (50,000)
ISOBUT
GASOLI
FURNA
ATMOSPHERIC & VACUUM FRACTIONATION (100,000)
WAX CUT
HEAVY DISTILATE
UNIFINING (HYDROTREATING) (35,000)
GASES
NAPHTHA
CATALYTIC CRACKING
REDUCED CRUDE

NOTE:
NUMBERS IN PARENTHESES REPRESENT PROCESS CAPACITIES IN BARRELS PER STREAM DAY (B/SD) IN A HYPOTHETICAL 100,000 B/SD REFINERY.

W.O. 30002

287-028 O - 68 (Face Reverse Of Appen. x B) No. 2

SUBPROCESS SERIES REPRESENTATIVE OF A TYPICAL TECH



ING
IG
GASES
GASOLINE
FURNACE OIL
COKE
G
H$_2$ MAKE-UP
MIXED AROMATICS
GASOLINE
TIC
ISOBUTANE & LT. OLEFINS
GASOLINE
FURNACE OIL
A
C CRACKING & REFORMING FEED
SOLID PHOSPHORIC ACID POLYMERIZATION (1,000)
PROPANE & BUTANE
GASOLINE
SULFURIC ACID ALKYLATION (6,000)
PROPANE & BUTANE
ALKYLATE
AROMATICS
SOLVENT REFINING
UDEX (2,500)
FURFURAL REFINING (3,500)
BENZE
SEPAR
AROMA
RAFFIN
SOLVENT DEWAXING (MEK) (4,000)
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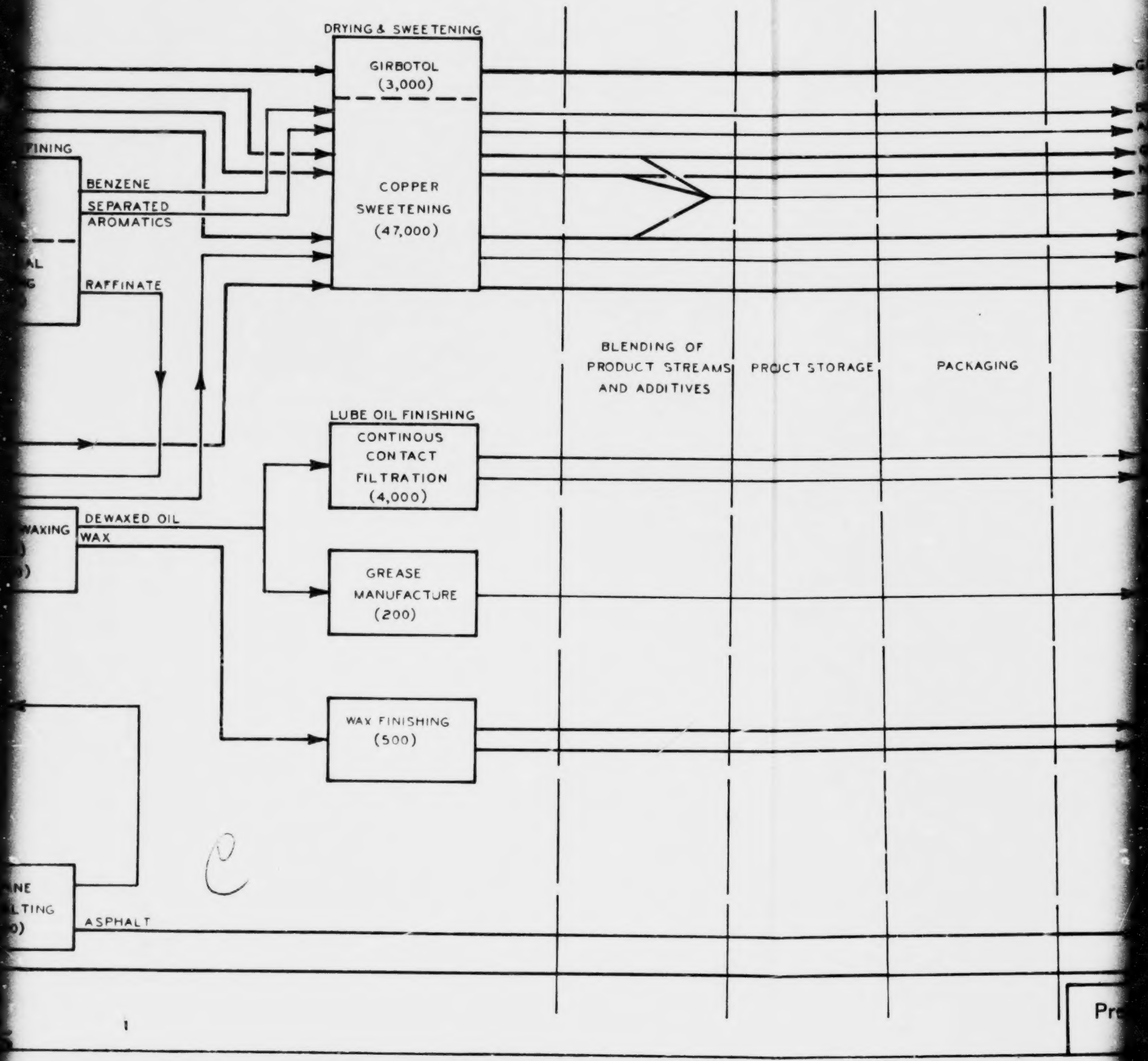
WAX
DEASPHALTED OIL
PROPANE DEASPHALTING (3,000)
ASPH

B

L TECHNOLOGY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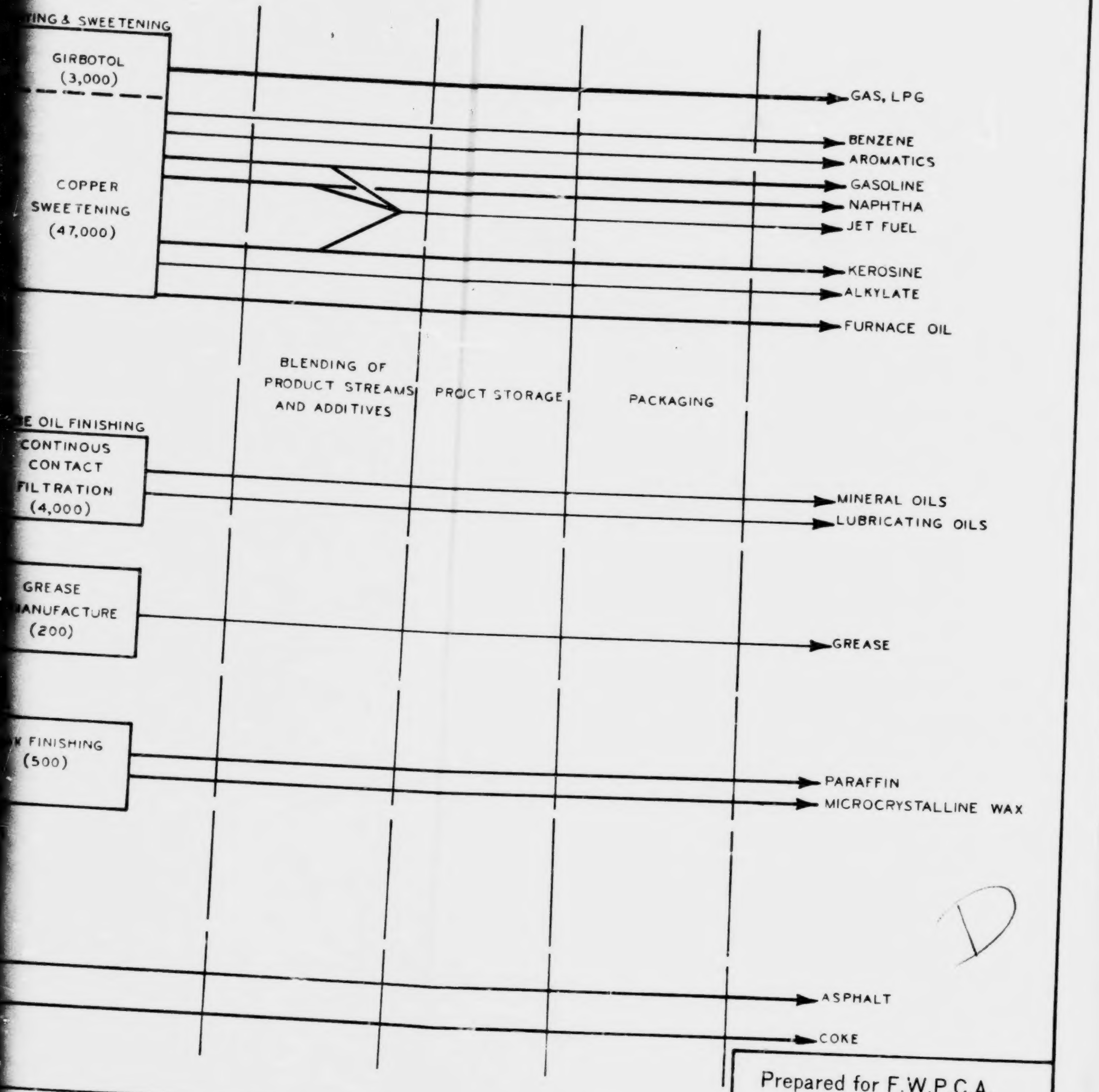
RAFFINATE
BLENDING OF PRODUCT STREAMS AND ADDITIVES
PRODUCT STORAGE
PACKAGING
LUBE OIL FINISHING
CONTINOUS CONTACT FILTRATION (4,000)
WAXING
DEWAXED OIL
WAX
GREASE MANUFACTURE (200)
WAX FINISHING (500)
C
INE
LTING
0)
ASPHALT
1
Pr

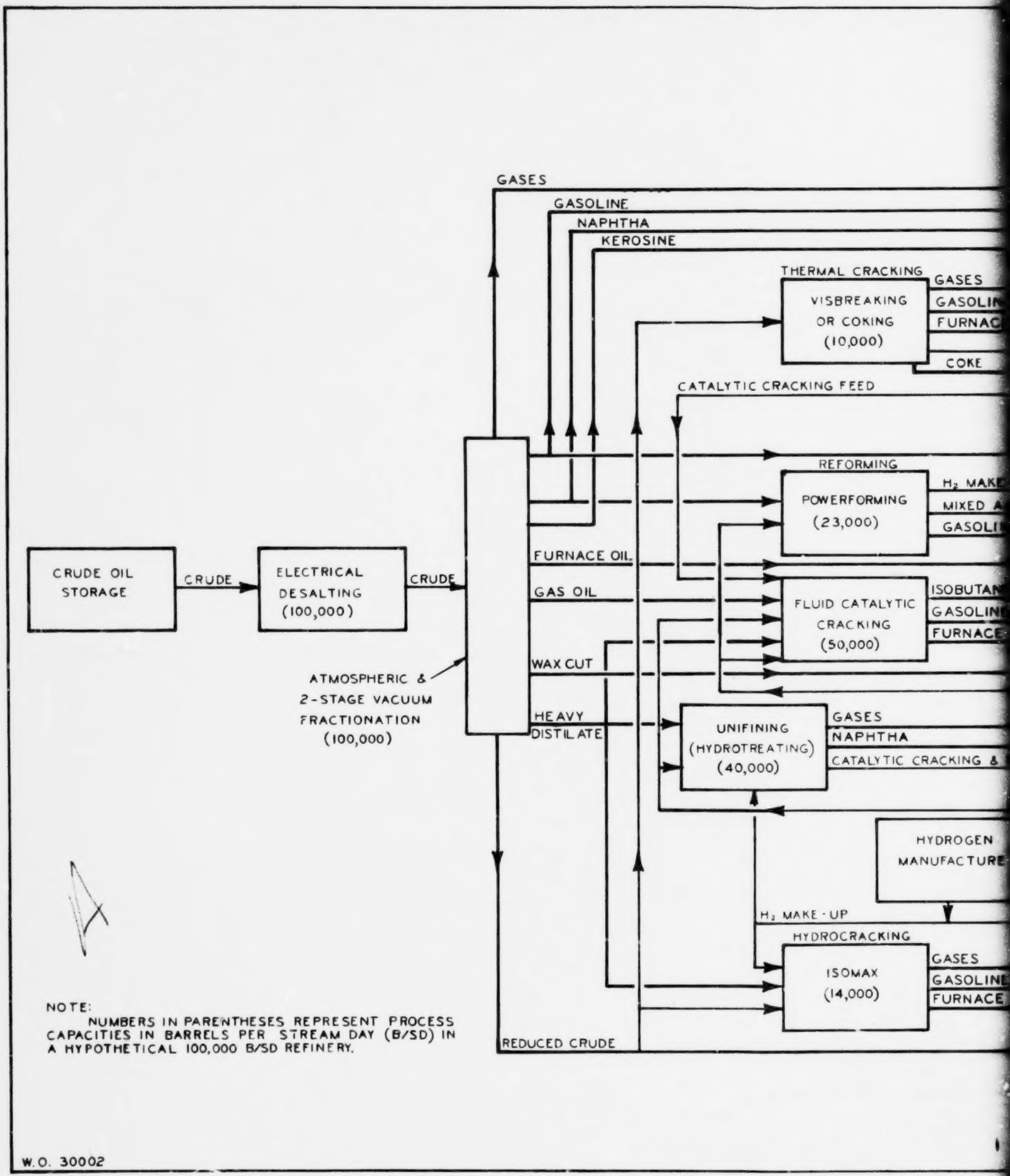


ING & SWEETENING
GIRBOTOL
(3,000)
COPPER
SWEETENING
(47,000)
GAS, LPG
BENZENE
AROMATICS
GASOLINE
NAPHTHA
JET FUEL
KEROSINE
ALKYLATE
FURNACE OIL
BLENDING OF
PRODUCT STREAMS
AND ADDITIVES
PROCT STORAGE
PACKAGING
E OIL FINISHING
CONTINOUS
CONTACT
FILTRATION
(4,000)
MINERAL OILS
LUBRICATING OILS
GREASE
ANUFACTURE
(200)
GREASE
FINISHING
(500)
PARAFFIN
MICROCRYSTALLINE WAX
ASPHALT
COKE

D

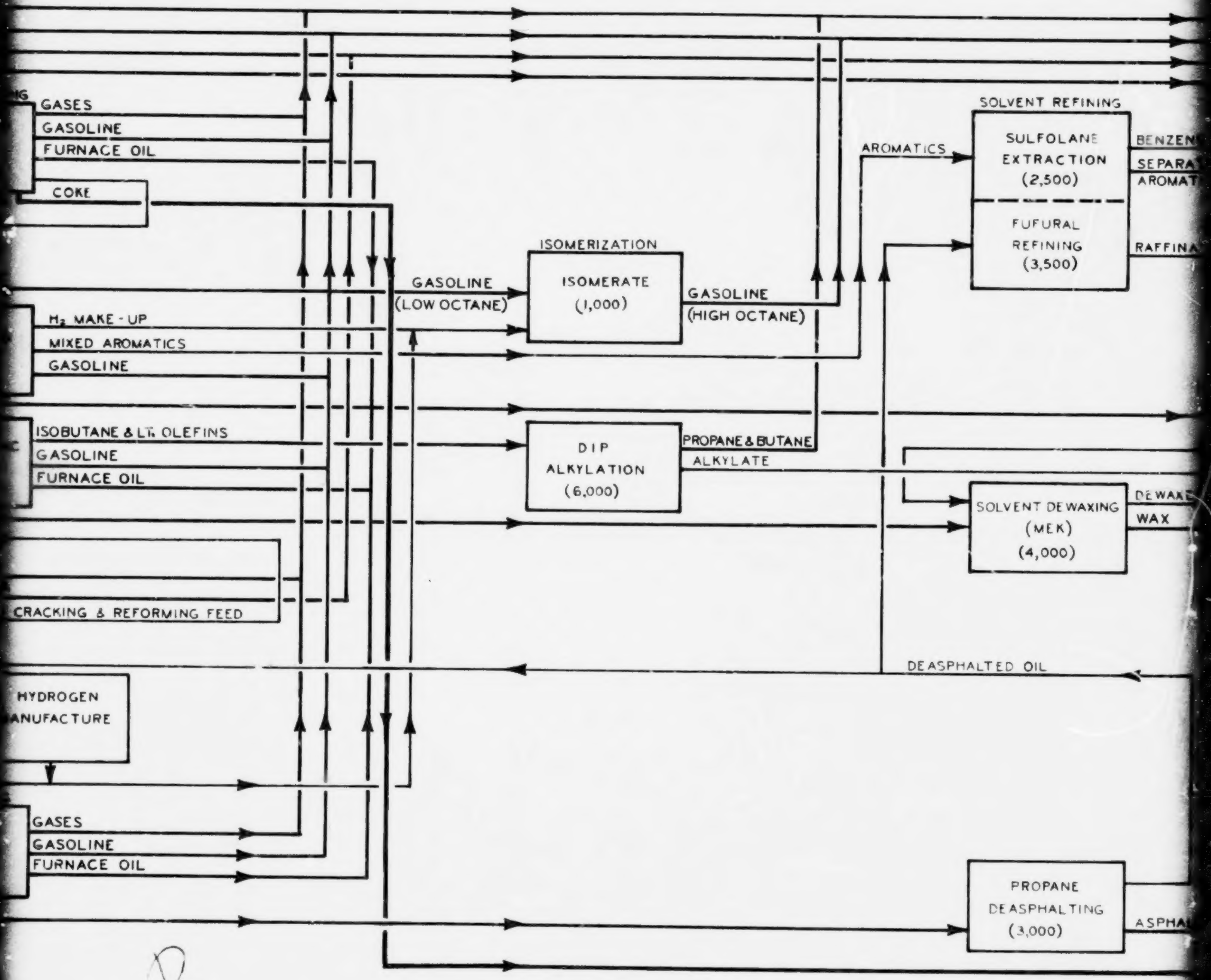
Prepared for F.W.P.C.A.

FIGURE 2


GASES
GASOLINE
NAPHTHA
KEROSINE
THERMAL CRACKING
VISBREAKING OR COKING (10,000)
GASES
GASOLIN
FURNAC
COKE
CATALYTIC CRACKING FEED
REFORMING
POWERFORMING (23,000)
H₂ MAKE
MIXED A
GASOLI
CRUDE OIL STORAGE
CRUDE
ELECTRICAL DESALTING (100,000)
CRUDE
FURNACE OIL
GAS OIL
FLUID CATALYTIC CRACKING (50,000)
ISOBUTAN
GASOLINE
FURNACE
WAX CUT
ATMOSPHERIC & 2-STAGE VACUUM FRACTIONATION (100,000)
HEAVY DISTILATE
UNIFINING (HYDROTREATING) (40,000)
GASES
NAPHTHA
CATALYTIC CRACKING &
HYDROGEN MANUFACTURE
H₂ MAKE-UP
HYDROCRACKING
ISOMAX (14,000)
GASES
GASOLINE
FURNACE
REDUCED CRUDE
W.O. 30002

NOTE:
NUMBERS IN PARENTHESES REPRESENT PROCESS CAPACITIES IN BARRELS PER STREAM DAY (B/SD) IN A HYPOTHETICAL 100,000 B/SD REFINERY.

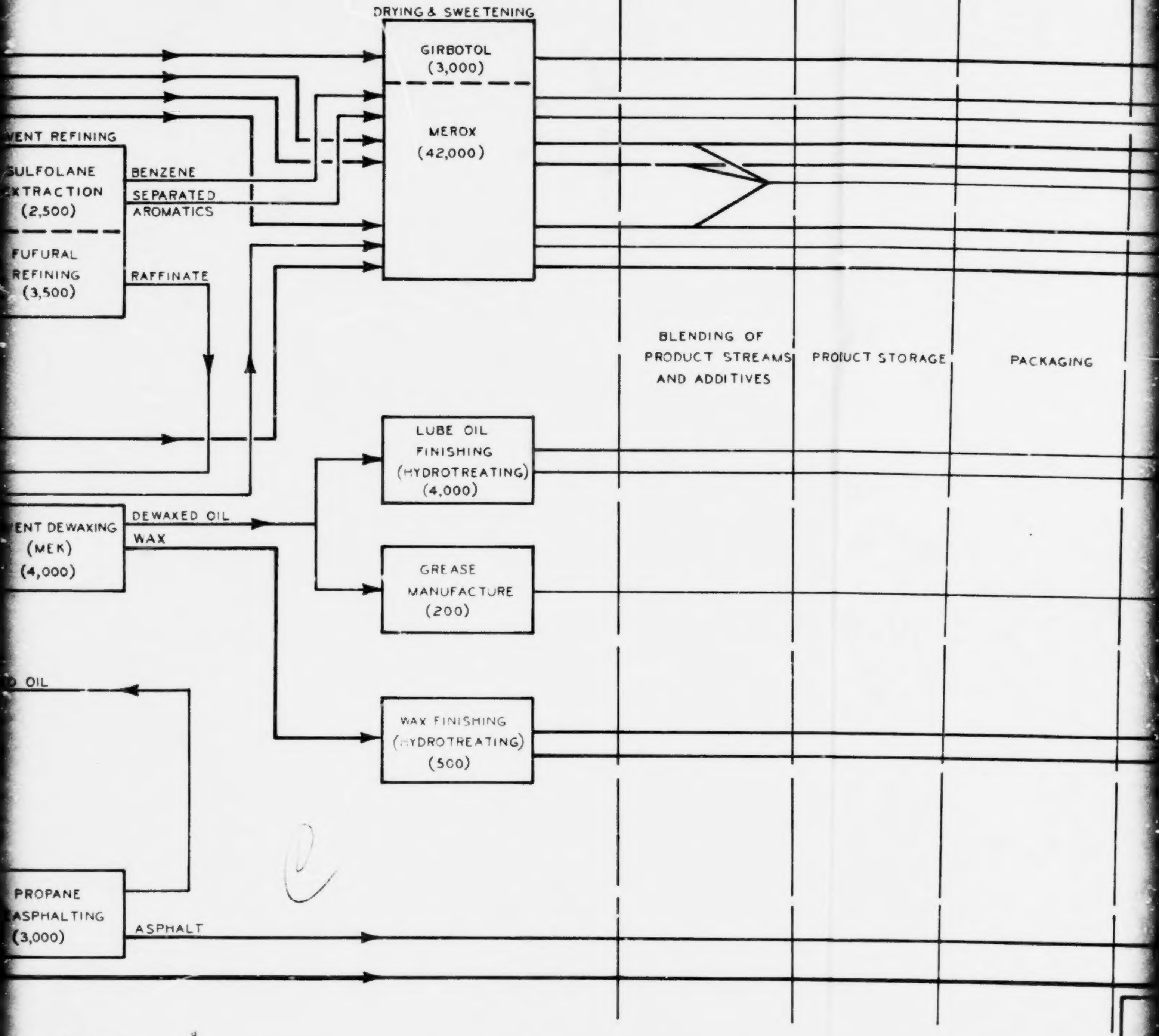
SUBPROCESS SERIES REPRESENTATIVE OF A NEWER TECHN

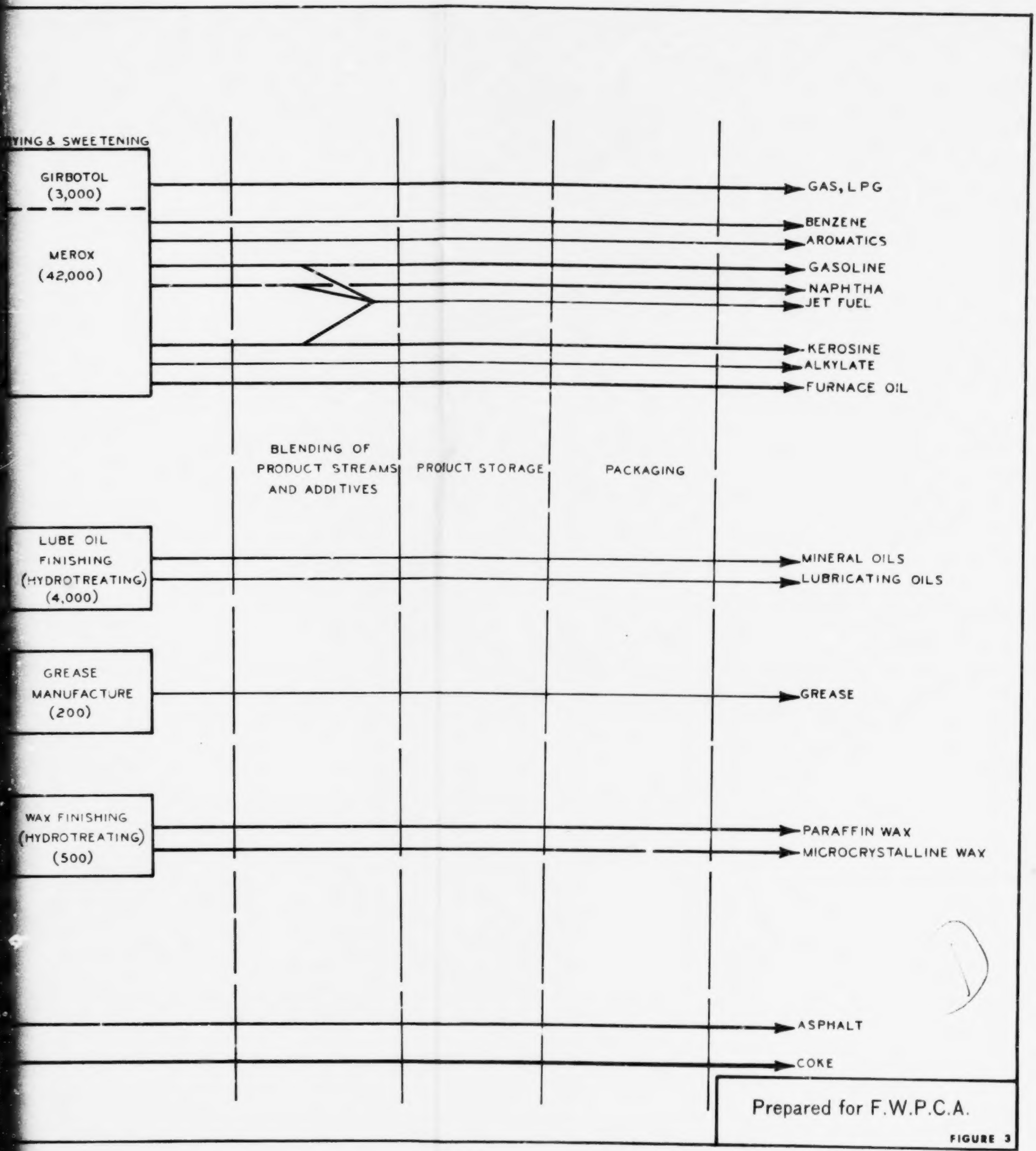


GASES
GASOLINE
FURNACE OIL
COKE
SOLVENT REFINING
AROMATICS
SULFOLANE EXTRACTION (2,500)
BENZEN
SEPARA
AROMAT
FUFURAL REFINING (3,500)
RAFFINA
ISOMERIZATION
GASOLINE (LOW OCTANE)
ISOMERATE (1,000)
GASOLINE (HIGH OCTANE)
H_2 MAKE - UP
MIXED AROMATICS
GASOLINE
ISOBUTANE & LT. OLEFINS
GASOLINE
FURNACE OIL
DIP ALKYLATION (6,000)
PROPANE & BUTANE
ALKYLATE
SOLVENT DEWAXING (MEK) (4,000)
DEWAX
WAX
CRACKING & REFORMING FEED
DEASPHALTED OIL
HYDROGEN
ANUFACTURE
GASES
GASOLINE
FURNACE OIL
PROPANE DEASPHALTING (3,000)
ASPHA

B

WER TECHNOLOGY

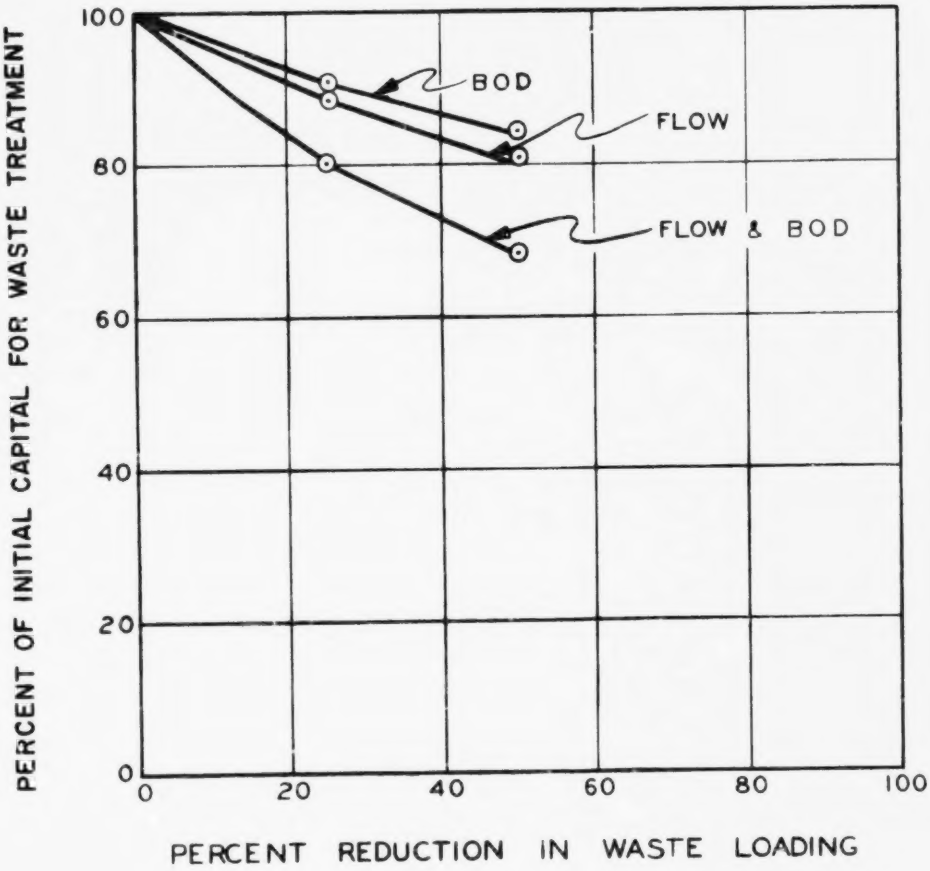

DRYING & SWEETENING
GIRBOTOL
(3,000)
MEROX
(42,000)
VENT REFINING
SULFOLANE
EXTRACTION
(2,500)
BENZENE
SEPARATED
AROMATICS
FUFURAL
REFINING
(3,500)
RAFFINATE
BLENDING OF
PRODUCT STREAMS
AND ADDITIVES
PROIUCT STORAGE
PACKAGING
LUBE OIL
FINISHING
(HYDROTREATING)
(4,000)
VENT DEWAXING
(MEK)
(4,000)
DEWAXED OIL
WAX
GREASE
MANUFACTURE
(200)
D OIL
WAX FINISHING
(HYDROTREATING)
(500)
PROPANE
ASPHALTING
(3,000)
ASPHALT


YING & SWEETENING
GIRBOTOL
(3,000)
MEROX
(42,000)
GAS, LPG
BENZENE
AROMATICS
GASOLINE
NAPHTHA
JET FUEL
KEROSINE
ALKYLATE
FURNACE OIL
BLENDING OF PRODUCT STREAMS AND ADDITIVES
PROIUCT STORAGE
PACKAGING
LUBE OIL FINISHING (HYDROTREATING) (4,000)
MINERAL OILS
LUBRICATING OILS
GREASE MANUFACTURE (200)
GREASE
WAX FINISHING (HYDROTREATING) (500)
PARAFFIN WAX
MICROCRYSTALLINE WAX
ASPHALT
COKE

Prepared for F.W.P.C.A.

FIGURE 3

EFFECT OF IN PLANT WASTE LOAD REDUCTION ON CAPITAL COST FOR HIGH DEGREE OF TREATMENT FOR TYPICAL 100,000 B P S D PETROLEUM REFINERY



Prepared for F.W.P.C.A.	DRAWN A W J	SCALE	FIG. NO. 4
	DATE 9 - 22	W.O. NO. 300-02	

2DF4 73489

CRUDE DESALTING
(ELECTROSTATIC DESALTING)

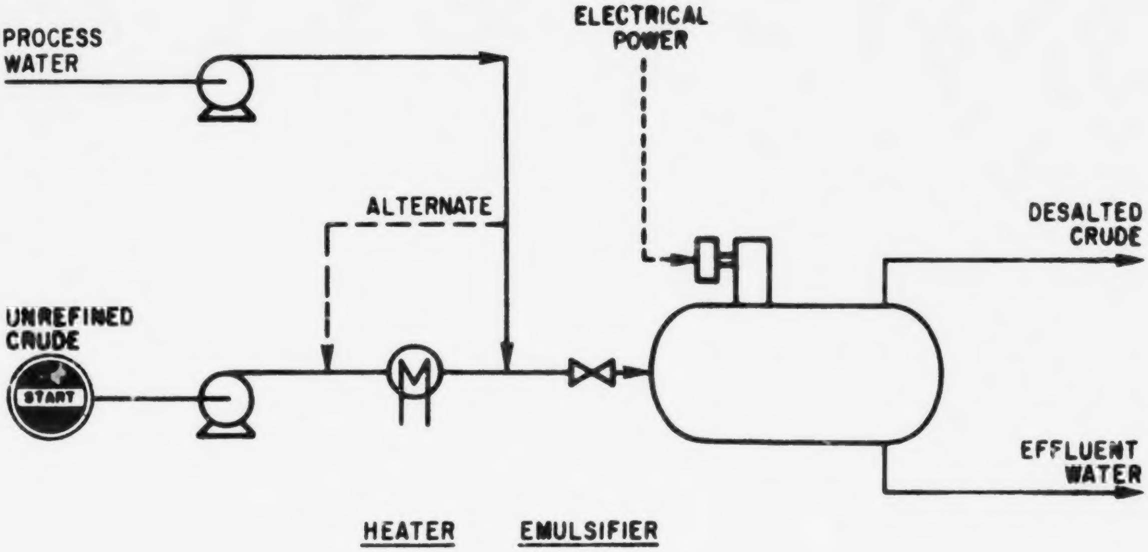

PROCESS WATER
ELECTRICAL POWER
ALTERNATE
DESALTED CRUDE
UNREFINED CRUDE
START
EFFLUENT WATER
HEATER
EMULSIFIER

FIGURE 5

HYDROCARBON PROCESSING 1966

CRUDE FRACTIONATION
(CRUDE DISTILLATION, THREE STAGES)

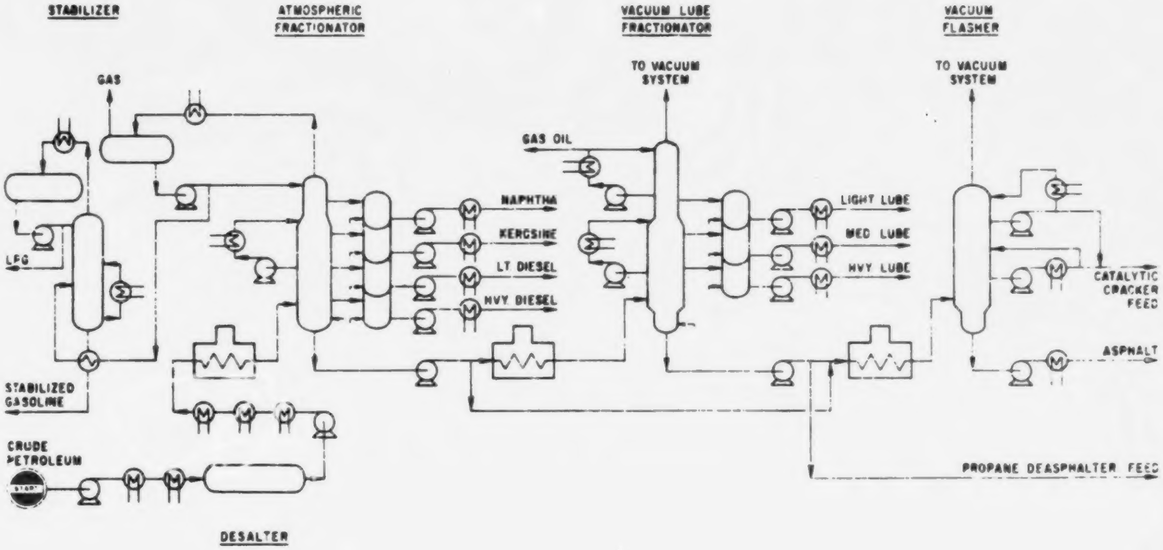

STABILIZER
ATMOSPHERIC FRACTIONATOR
VACUUM LUBE FRACTIONATOR
VACUUM FLASHER
GAS
TO VACUUM SYSTEM
TO VACUUM SYSTEM
GAS OIL
NAPHTHA
KEROSINE
LT DIESEL
HVY DIESEL
LIGHT LUBE
MED LUBE
HVY LUBE
CATALYTIC CRACKER FEED
ASPHALT
LPG
STABILIZED GASOLINE
CRUDE PETROLEUM
START
PROPANE DEASPHALTER FEED
DESALTER

FIGURE 6

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

THERMAL CRACKING
(DELAYED COKING)

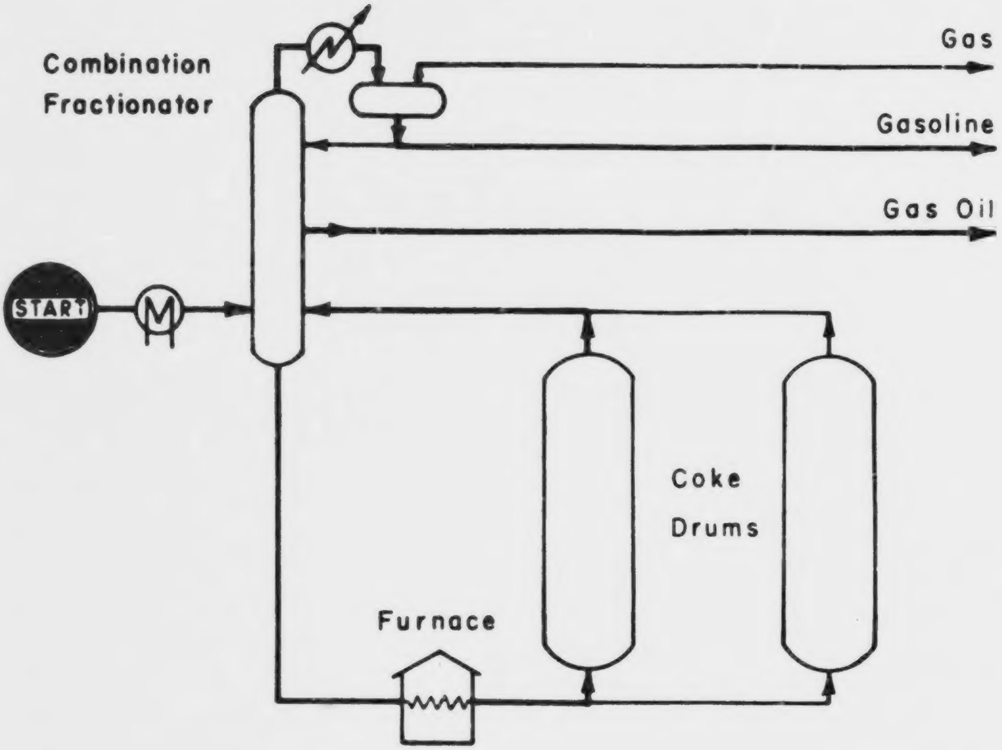

Combination
Fractionator
Gas
Gasoline
Gas Oil
START
M
Coke
Drums
Furnace

FIGURE 7

HYDROCARBON PROCESSING 1966

THERMAL CRACKING (VISBREAKING)

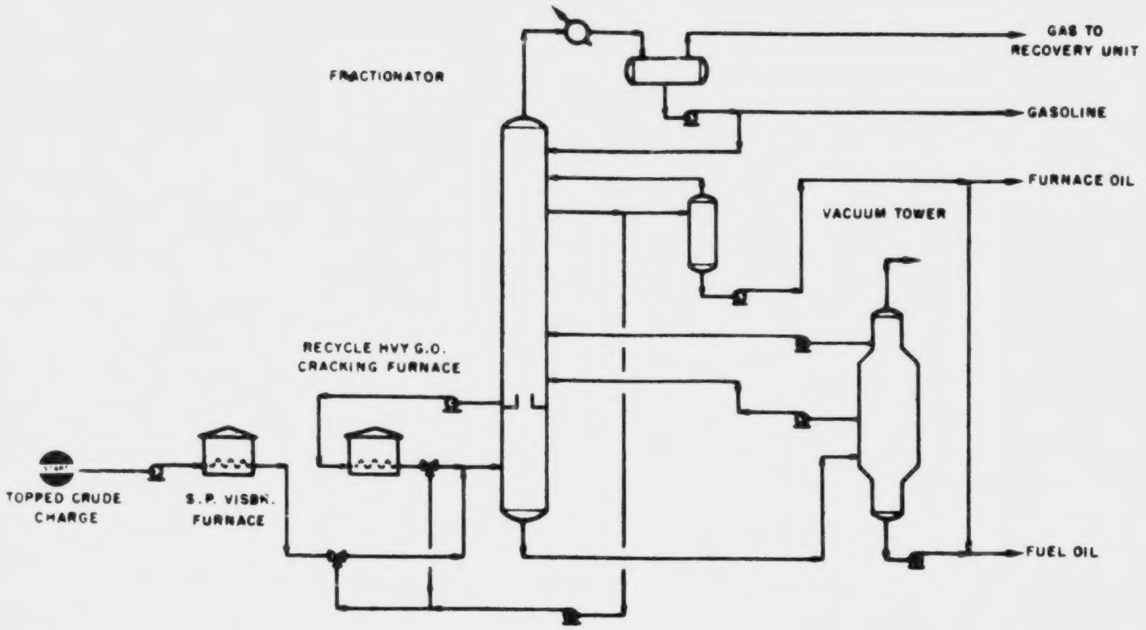

GAS TO RECOVERY UNIT
FRACTIONATOR
GASOLINE
FURNACE OIL
VACUUM TOWER
RECYCLE HVY G.O. CRACKING FURNACE
TOPPED CRUDE CHARGE
S.P. VISBK. FURNACE
FUEL OIL

FIGURE 8

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

CATALYTIC CRACKING
(FLUID CATALYTIC CRACKING)

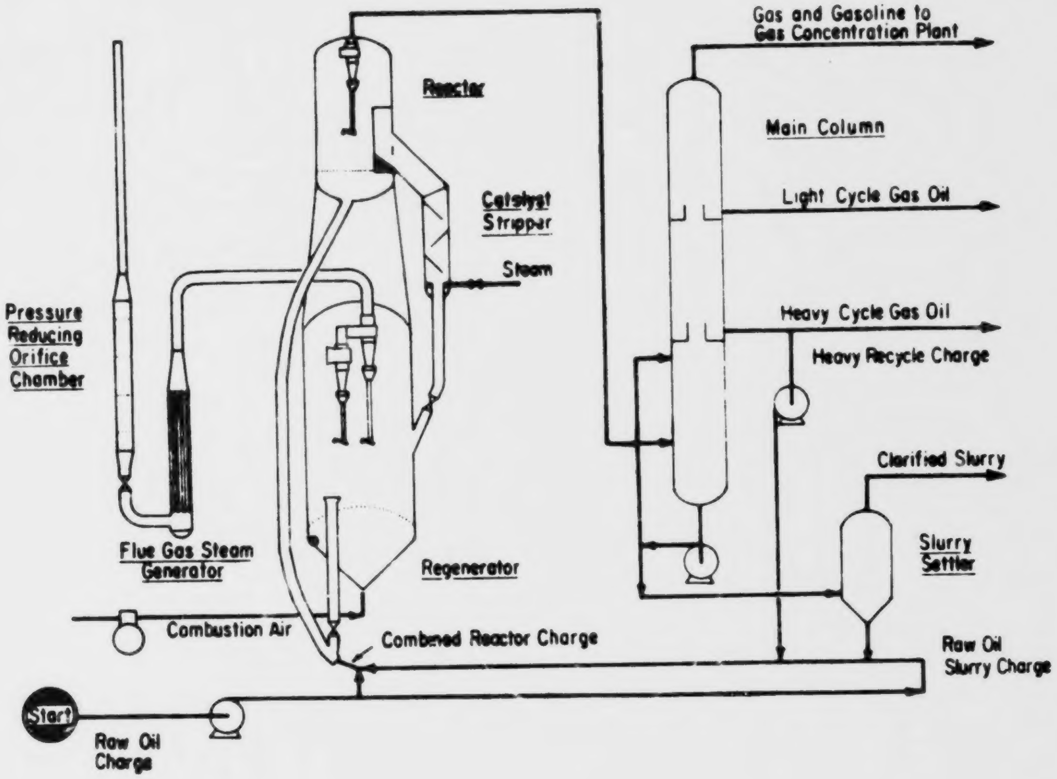

Gas and Gasoline to Gas Concentration Plant
Reactor
Main Column
Catalyst Stripper
Light Cycle Gas Oil
Steam
Pressure Reducing Orifice Chamber
Heavy Cycle Gas Oil
Heavy Recycle Charge
Clarified Slurry
Flue Gas Steam Generator
Regenerator
Slurry Settler
Combustion Air
Combined Reactor Charge
Raw Oil Slurry Charge
Start
Raw Oil Charge

FIGURE 9

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

HYDROCRACKING (ISOMAX)

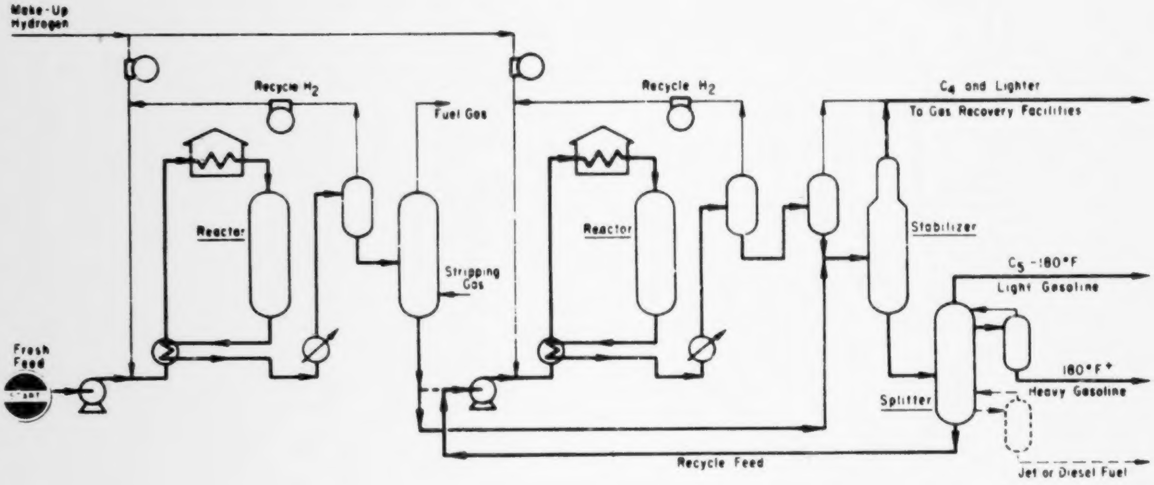

Make-Up Hydrogen
Recycle H_2
Fuel Gas
Reactor
Stripping Gas
Fresh Feed
START
Recycle H_2
Reactor
C_4 and Lighter
To Gas Recovery Facilities
Stabilizer
C_5 -180°F
Light Gasoline
180°F+
Heavy Gasoline
Splitter
Recycle Feed
Jet or Diesel Fuel

FIGURE 10

HYDROCARBON PROCESSING 1966

POLYMERIZATION
(BULK ACID POLYMERIZATION)

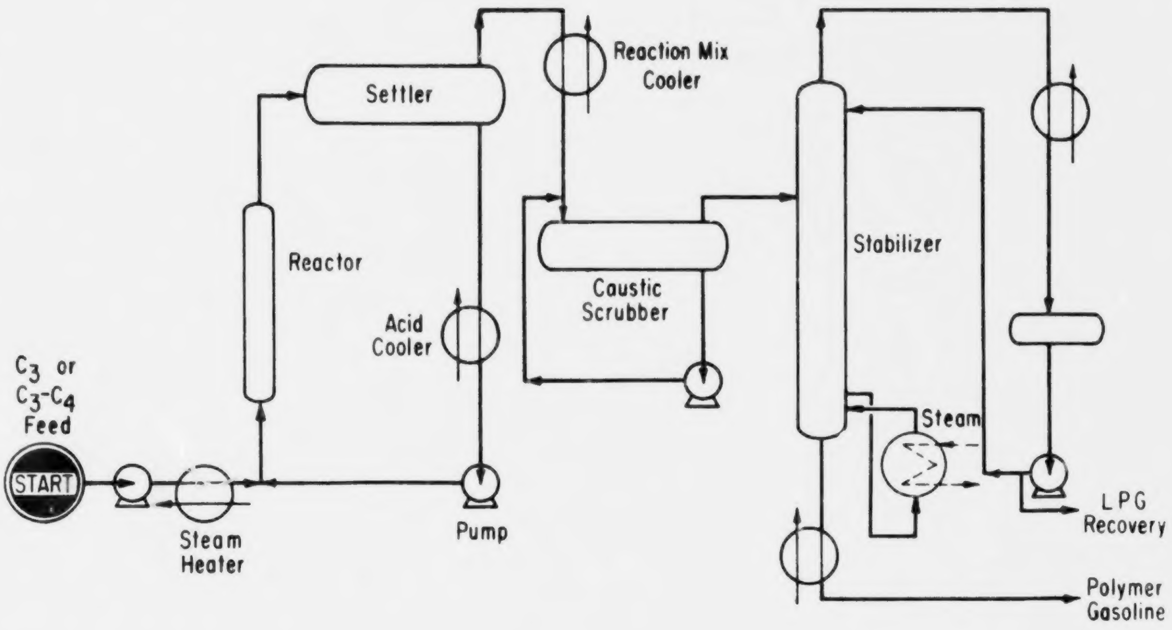

Reaction Mix Cooler
Settler
Reactor
Acid Cooler
Caustic Scrubber
Stabilizer
C_3 or C_3-C_4 Feed
START
Steam Heater
Pump
Steam
LPG Recovery
Polymer Gasoline

FIGURE 11

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

ALKYLATION
(CASCADE SULFURIC ACID ALKYLATION)

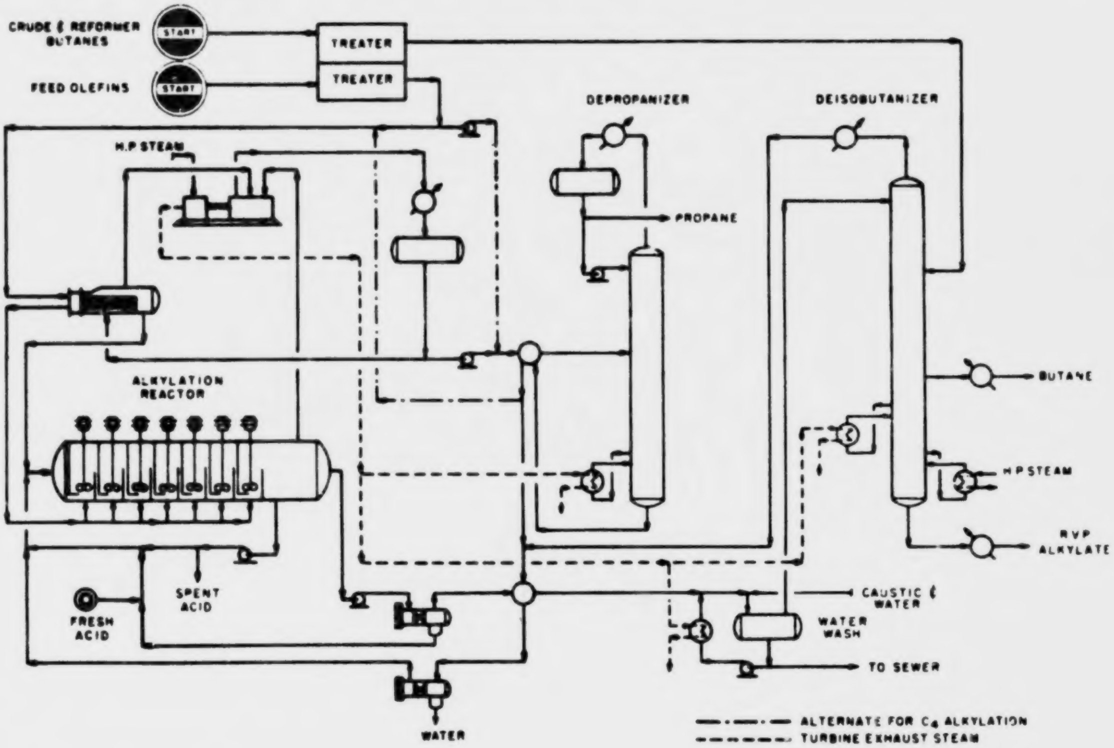

CRUDE & REFORMER BUTANES
START
FEED OLEFINS
START
TREATER
TREATER
DEPROPANIZER
DEISOBUTANIZER
H.P STEAM
PROPANE
ALKYLATION REACTOR
BUTANE
H.P STEAM
RVP ALKYLATE
SPENT ACID
FRESH ACID
CAUSTIC & WATER
WATER WASH
TO SEWER
WATER
ALTERNATE FOR C4 ALKYLATION
TURBINE EXHAUST STEAM

FIGURE 12

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

ISOMERIZATION
(ISOMERATE)

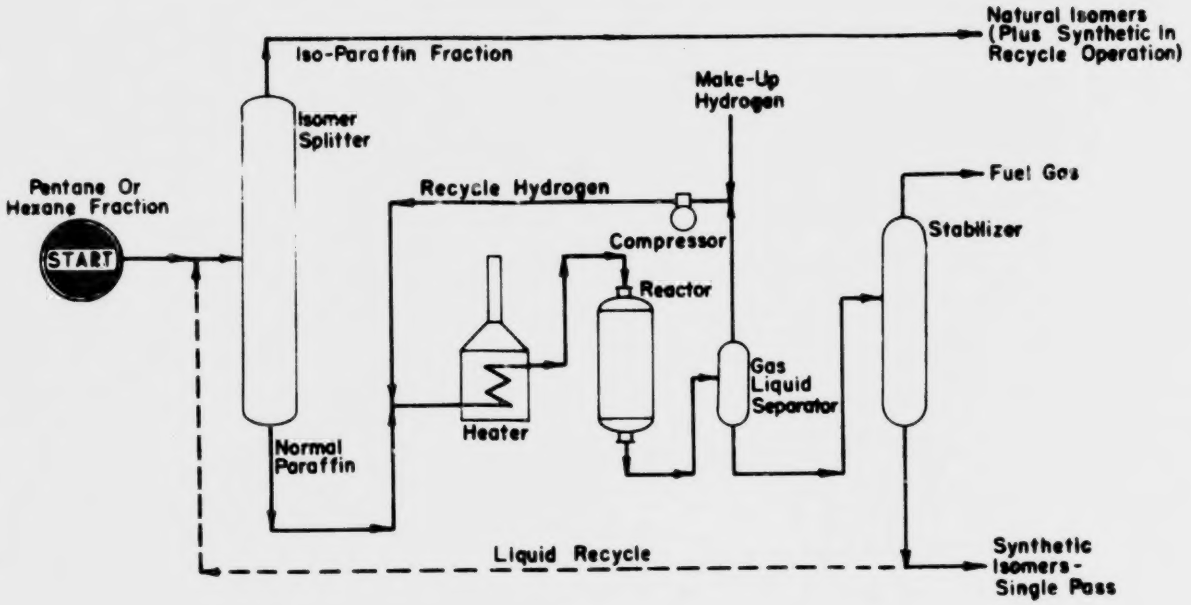

Natural Isomers (Plus Synthetic In Recycle Operation)
Iso-Paraffin Fraction
Make-Up Hydrogen
Isomer Splitter
Fuel Gas
Pentane Or Hexane Fraction
Recycle Hydrogen
START
Compressor
Stabilizer
Reactor
Gas Liquid Separator
Heater
Normal Paraffin
Liquid Recycle
Synthetic Isomers - Single Pass

FIGURE 13

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

SOLVENT REFINING
(FURFURAL REFINING)

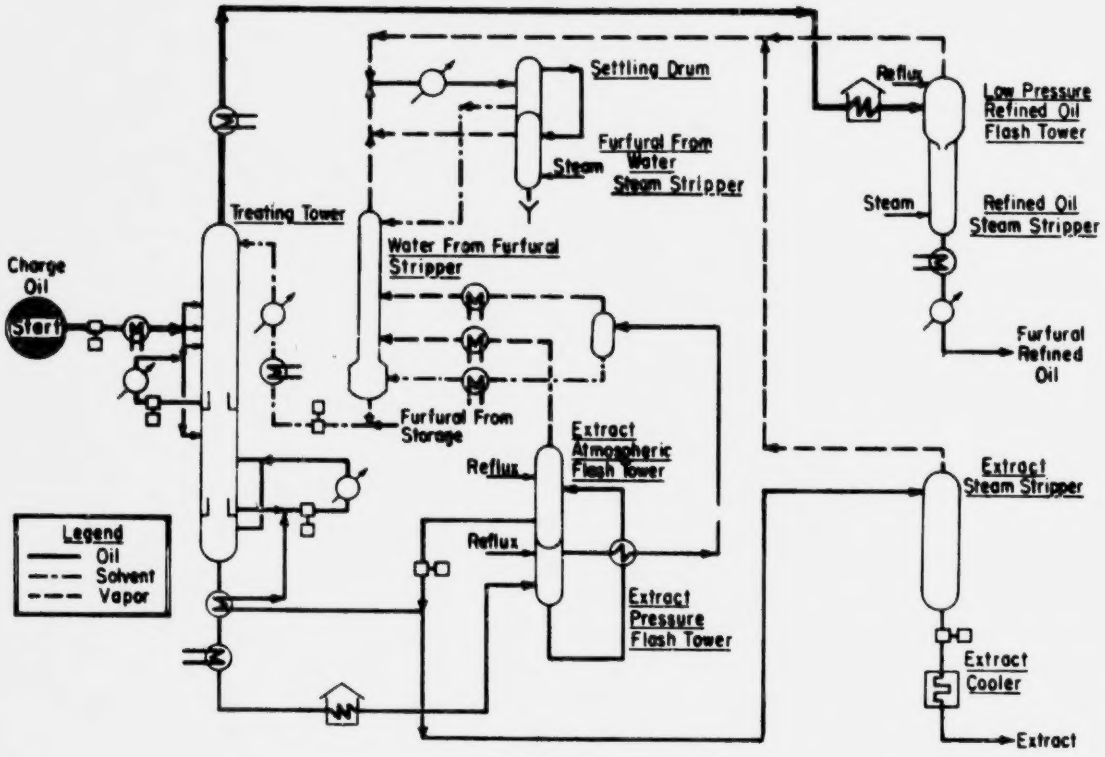

Settling Drum
Furfural From Water Steam Stripper
Steam
Reflux
Low Pressure Refined Oil Flash Tower
Steam
Refined Oil Steam Stripper
Treating Tower
Water From Furfural Stripper
Charge Oil
Start
Furfural Refined Oil
Furfural From Storage
Extract Atmospheric Flash Tower
Reflux
Reflux
Extract Steam Stripper
Legend
Oil
Solvent
Vapor
Extract Pressure Flash Tower
Extract Cooler
Extract

FIGURE 14

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

SOLVENT REFINING
(UDEX)

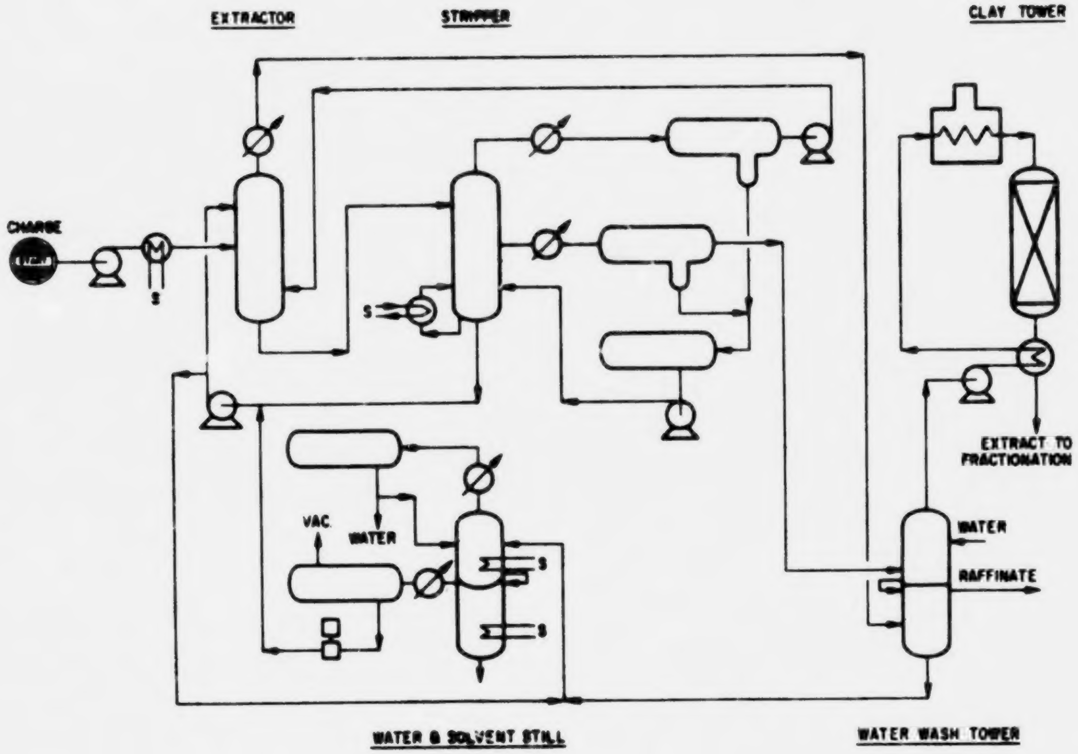

EXTRACTOR
STRIPPER
CLAY TOWER
CHARGE
S
S
VAC.
WATER
S
S
EXTRACT TO FRACTIONATION
WATER
RAFFINATE
WATER & SOLVENT STILL
WATER WASH TOWER

FIGURE 15

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

DEWAXING
(SOLVENT DEWAXING-MEK)

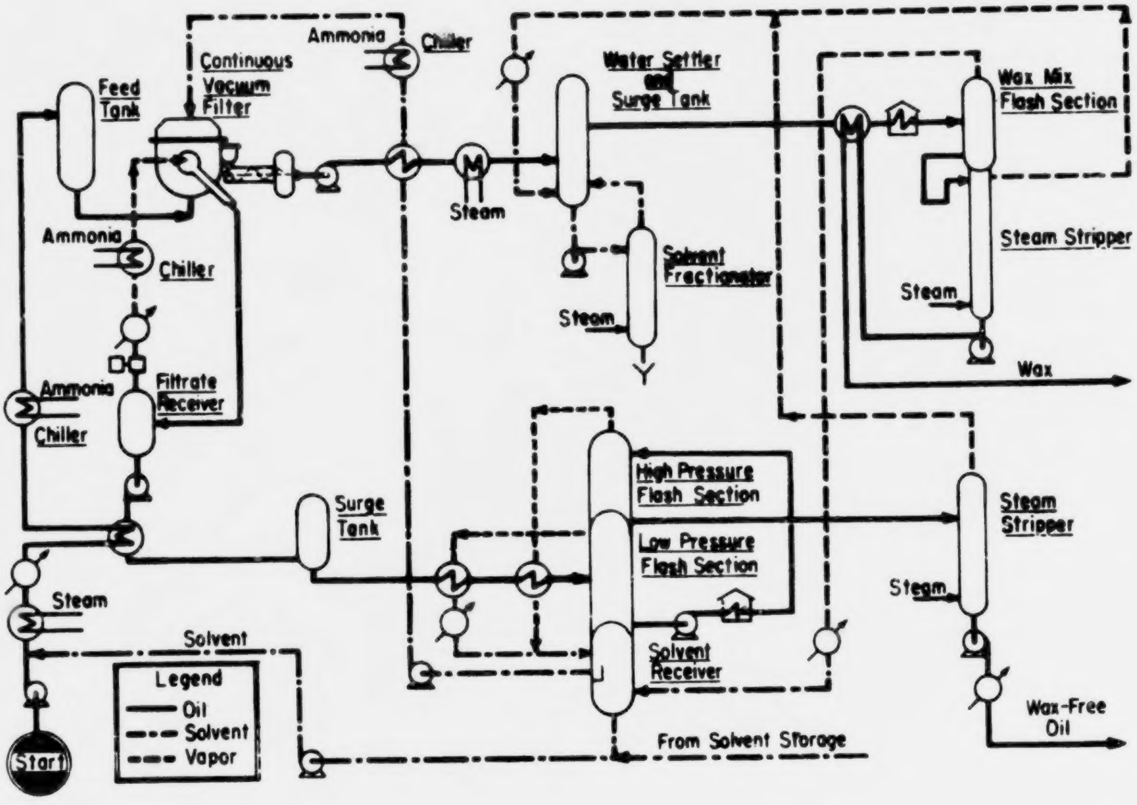

Ammonia
Chiller
Continuous Vacuum Filter
Feed Tank
Water Settler and Surge Tank
Wax Mix Flash Section
Steam
Ammonia
Chiller
Solvent Fractionator
Steam Stripper
Steam
Steam
Wax
Ammonia
Chiller
Filtrate Receiver
High Pressure Flash Section
Surge Tank
Low Pressure Flash Section
Steam Stripper
Steam
Steam
Solvent
Solvent Receiver
Legend
Oil
Solvent
Vapor
Start
Wax-Free Oil
From Solvent Storage

FIGURE 16

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

HYDROTREATING
(UNIFINING)

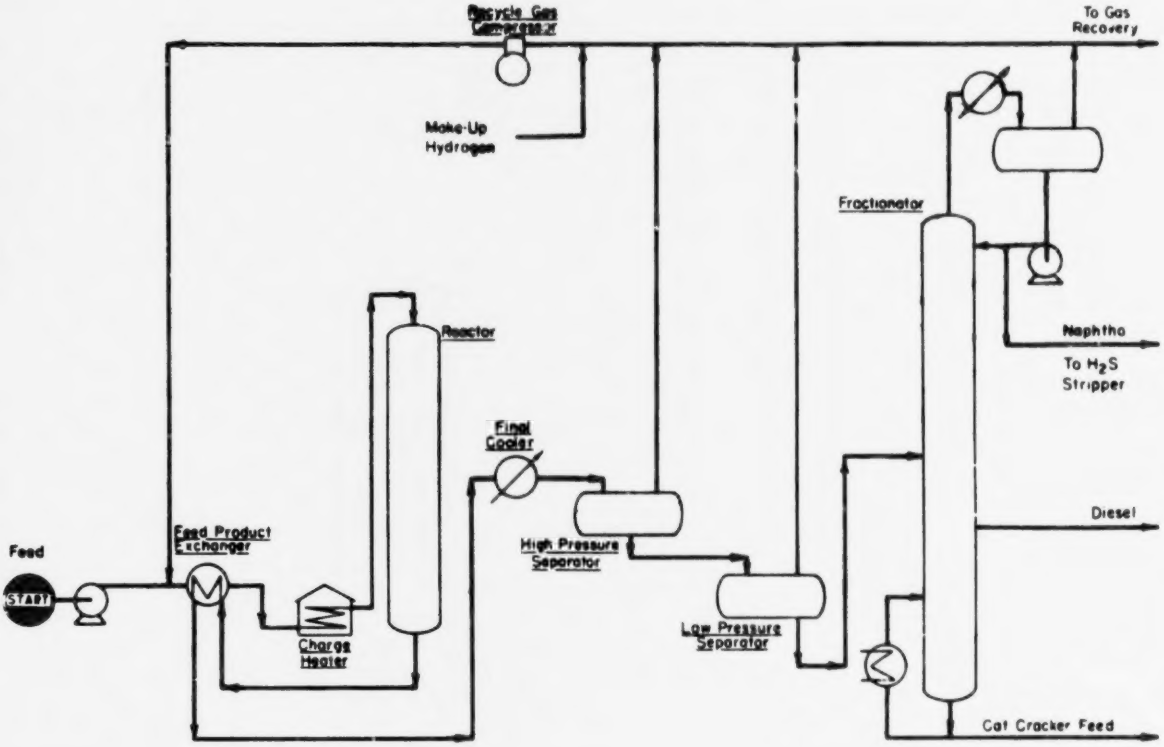

Recycle Gas Compressor
To Gas Recovery
Make-Up Hydrogen
Fractionator
Reactor
Naphtha
To H_2S Stripper
Final Cooler
Diesel
Feed
START
Feed Product Exchanger
Charge Heater
High Pressure Separator
Low Pressure Separator
Cat Cracker Feed

FIGURE 17

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

DEASPHALTING
(PROPANE DEASPHALTING AND FRACTIONATION)

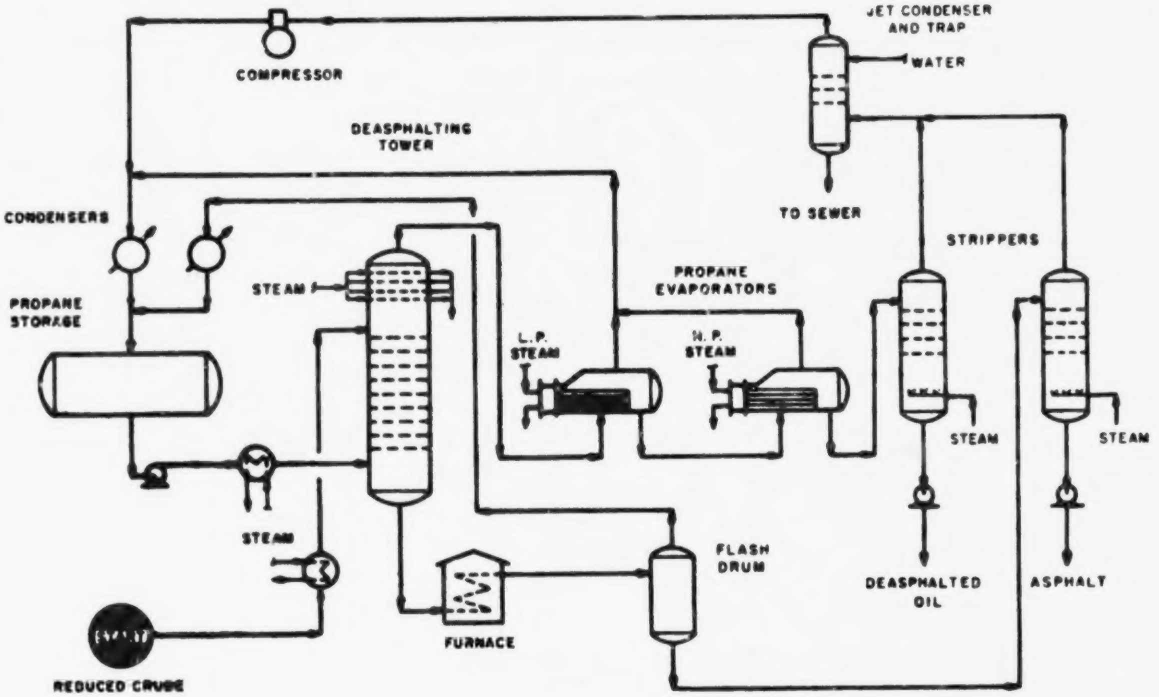

JET CONDENSER AND TRAP
WATER
COMPRESSOR
DEASPHALTING TOWER
TO SEWER
CONDENSERS
STRIPPERS
PROPANE EVAPORATORS
STEAM
PROPANE STORAGE
L.P. STEAM
H.P. STEAM
STEAM
STEAM
STEAM
FLASH DRUM
DEASPHALTED OIL
ASPHALT
FURNACE
REDUCED CRUDE

FIGURE 18

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

DRYING AND SWEETENING
(COPPER SWEETENING)

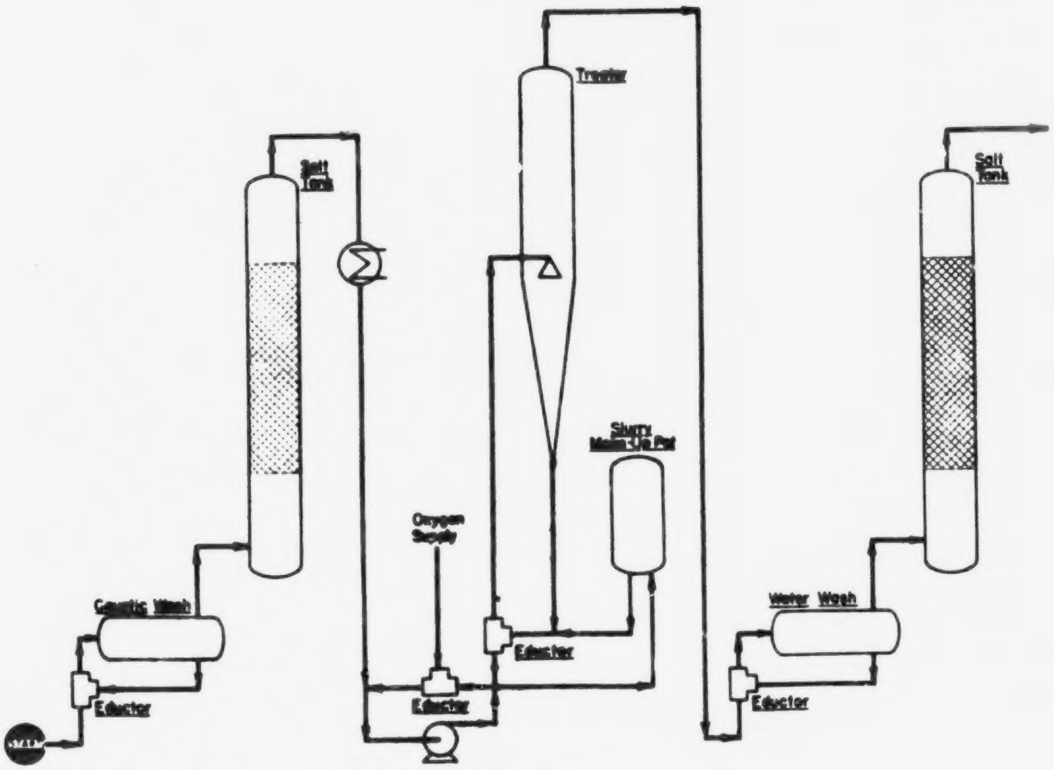

Treater
Salt Tank
Salt Tank
Slurry Make-Up Pot
Oxygen Supply
Caustic Wash
Eductor
Eductor
Eductor
Water Wash
Eductor

FIGURE 19

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

DRYING AND SWEETENING

(GIRBOTOL)

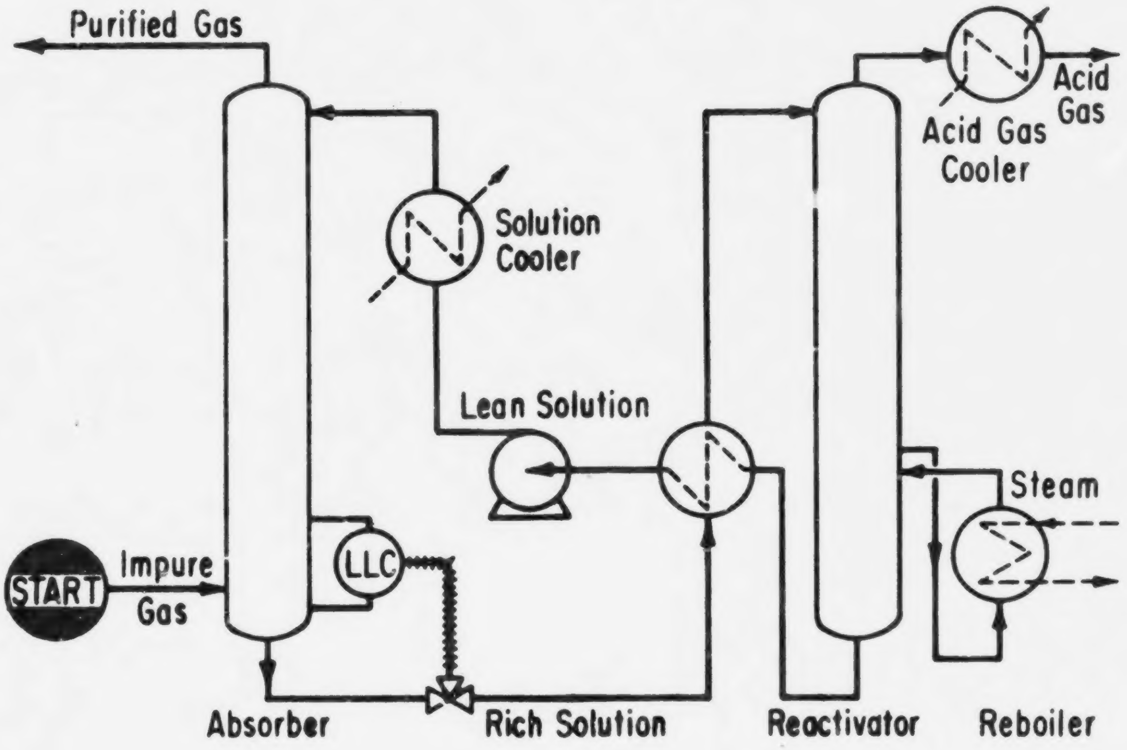

Purified Gas
Acid Gas
Acid Gas Cooler
Solution Cooler
Lean Solution
Steam
START
Impure Gas
LLC
Absorber
Rich Solution
Reactivator
Reboiler

FIGURE 20

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

WAX FINISHING
(WAX FRACTIONATION)

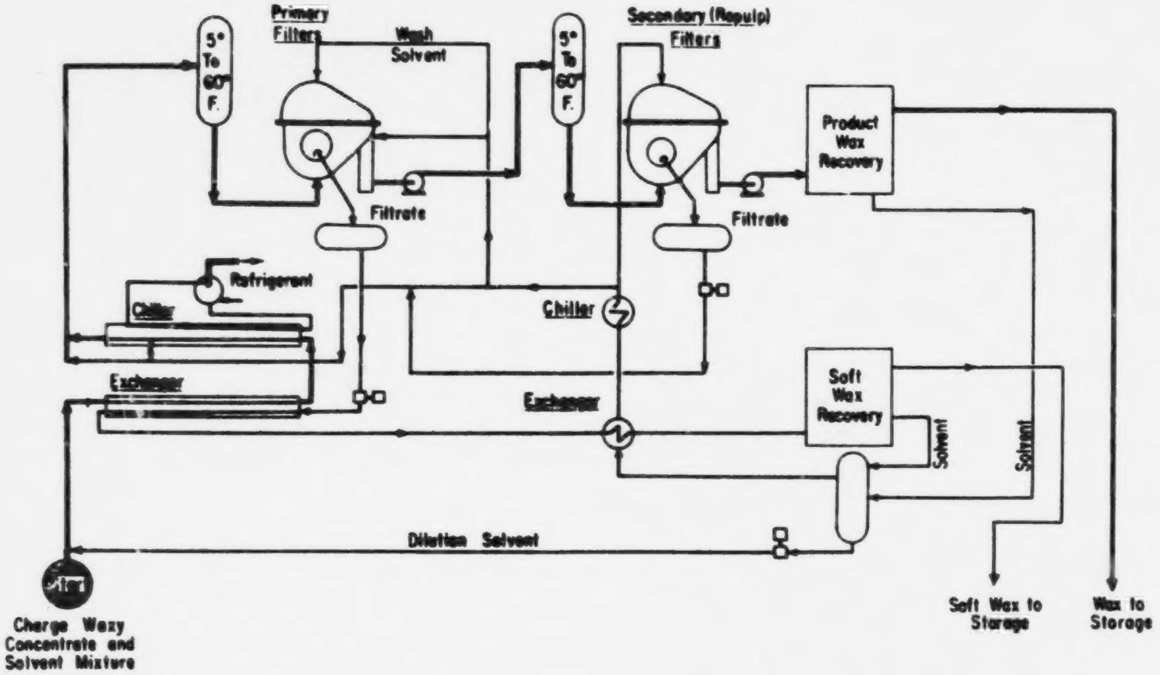

Primary Filters
Wash Solvent
5° To 60° F.
5° To 60° F.
Secondary (Repulp) Filters
Product Wax Recovery
Filtrate
Filtrate
Refrigerant
Chiller
Chiller
Exchanger
Exchanger
Soft Wax Recovery
Solvent
Solvent
Dilution Solvent
Charge Wazy Concentrate and Solvent Mixture
Soft Wax to Storage
Wax to Storage

FIGURE 21

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

GREASE MANUFACTURE
(GREASE MANUFACTURING)

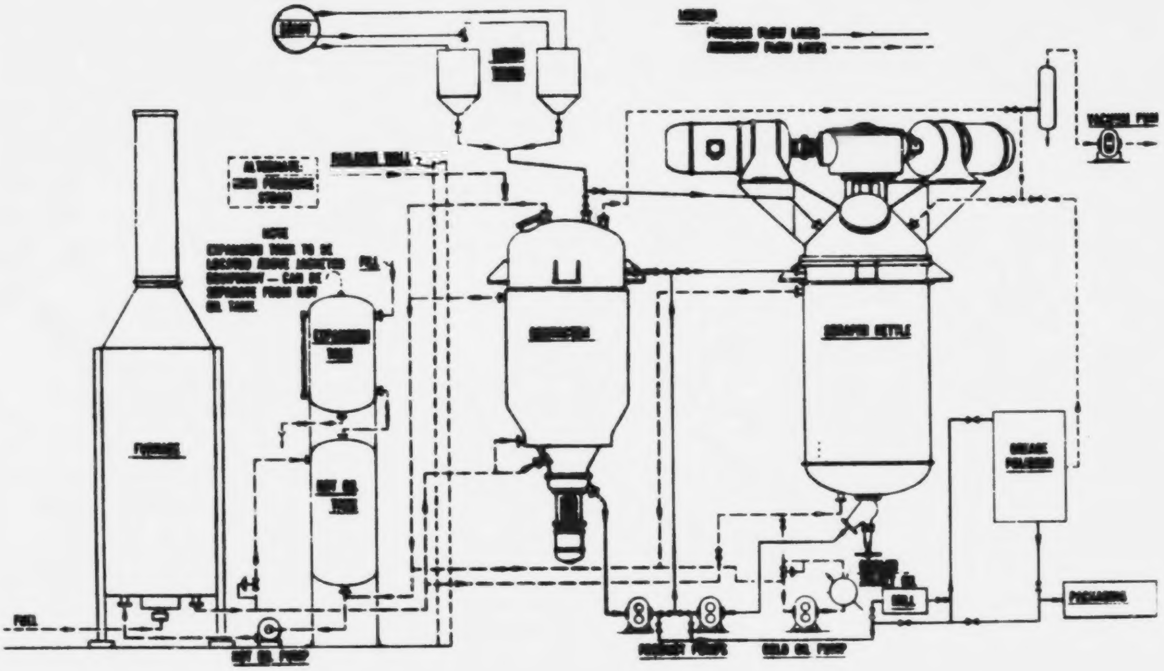

FURNACE
EXPANSION TANK
HOT OIL TANK
FILL
FUEL
HOT OIL PUMP
SCRAPER KETTLE
VACUUM PUMP
GREASE POLISHER
MILL
PACKAGING
PRODUCT PUMPS
COLD OIL PUMP

FIGURE 22

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

LUBE OIL FINISHING
(PERCOLATION FILTRATION)

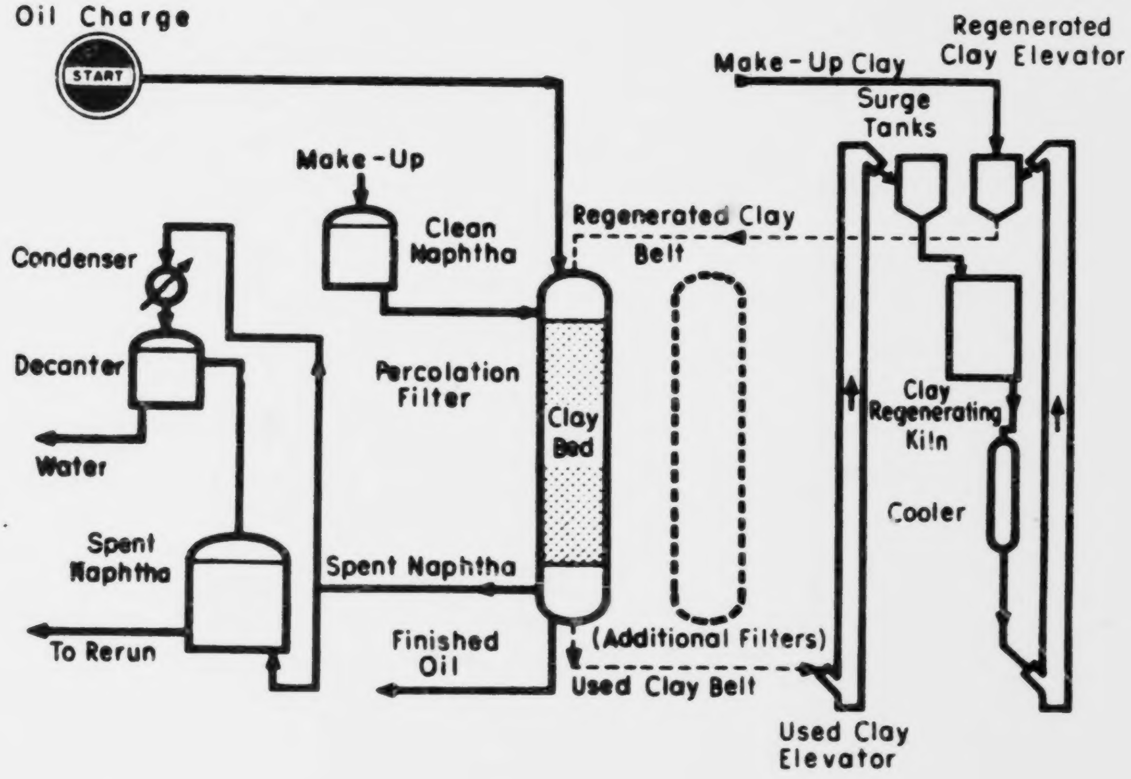

Oil Charge
START
Make-Up Clay
Regenerated Clay Elevator
Surge Tanks
Make-Up
Clean Naphtha
Regenerated Clay Belt
Condenser
Decanter
Percolation Filter
Clay Bed
Clay Regenerating Kiln
Water
Cooler
Spent Naphtha
Spent Naphtha
To Rerun
Finished Oil
(Additional Filters)
Used Clay Belt
Used Clay Elevator

FIGURE 23

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

HYDROGEN MANUFACTURE
(HYDROGEN, STEAM REFORMING)

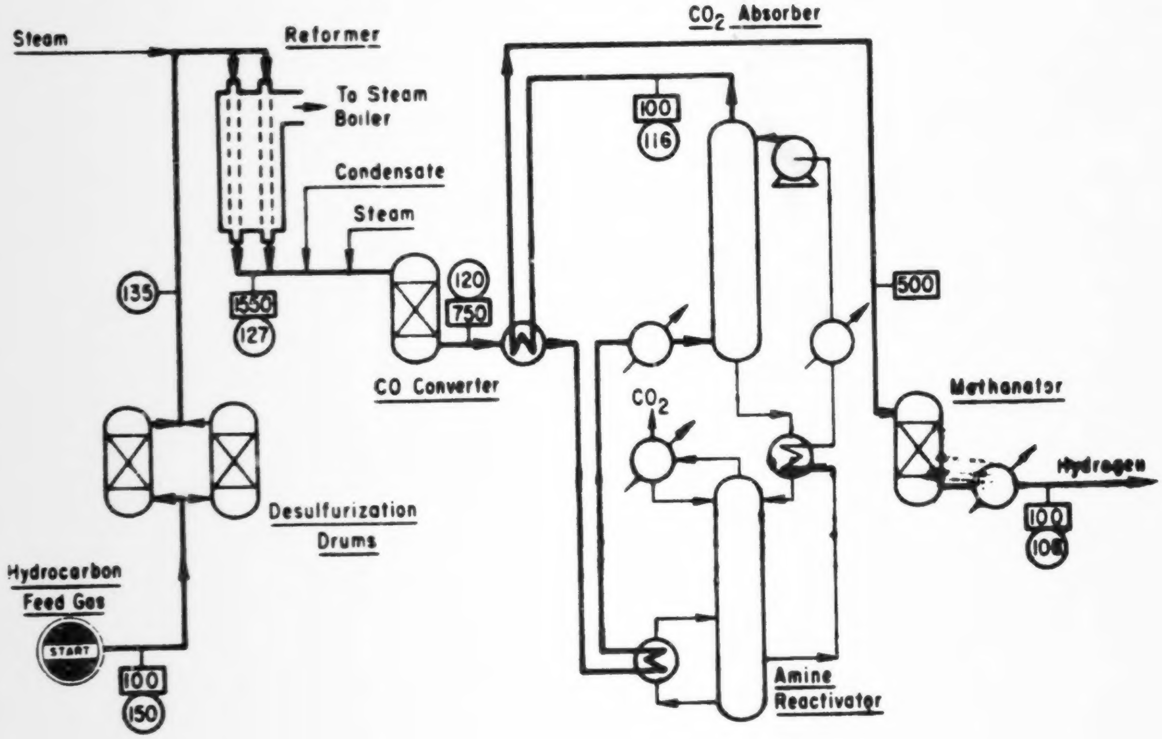

Steam
Reformer
To Steam Boiler
Condensate
Steam
135
1550
127
120
750
CO Converter
CO2 Absorber
100
116
500
CO2
Methanator
Hydrogen
100
106
Desulfurization Drums
Hydrocarbon Feed Gas
START
100
150
Amine Reactivator

FIGURE 24

Prepared for F.W.P.C.A.

HYDROCARBON PROCESSING 1966

APPENDIX C

GLOSSARY AND ABBREVIATIONS

GLOSSARY

Aerobic - In the presence of oxygen.

Aquatic Life - All living forms in natural waters, including plants, fish, shellfish, and lower forms of animal life.

Aromatics - Hydrocarbon compounds involving a 6-carbon, benzene ring structure.

Ballast Water - Water used as ballast by oil tankers.

Biochemical Oxygen Demand - Oxygen used by bacteria in consuming a waste substance.

By-Product - Material which, if recovered, would accrue some economic benefit but not necessarily enough to cover the cost of recovery.

Catalyst - A substance which can change the rate of a chemical reaction but which is not itself involved in the reaction.

Cetane - A straight chain, 16-carbon hydrocarbon, used as a standard for performance of diesel fuels.

Chemical Oxygen Demand - Oxygen consumed through chemical oxidation of a waste.

Direct-Fired Heater - A heater in which heat is supplied by combustion, as distinguished from a heat exchanger where heat is supplied by a hot liquid or gas.

Emulsion - A liquid system in which one liquid is finely dispersed in another liquid in such a manner that the two will not separate through the action of gravity alone.

End-of-Pipe Treatment - Treatment of overall refinery wastes, as distinguished from treatment at individual processing units.

Fractionator - A generally cylindrical tower in which a mixture of liquid components is vaporized and the components separated by carefully varying the temperature and sometimes pressure along the length of the tower.

Gasoline - A mixture of hydrocarbon compounds with a boiling range between 100 and 400°F.

Grease - A solid or semi-solid composition made up of animal fats, alkali, water, oil and various additives.

Hydrocarbon - A compound consisting of carbon and hydrogen.

Hydrogenation - The contacting of hydrocarbons with hydrogen gas at controlled temperatures and pressures for the purpose of obtaining saturated hydrocarbons and/or removing various impurities such as sulfur and nitrogen.

Isomer - A chemical compound that has the same number, and kinds of atoms as another compound, but a different structural arrangement of the atoms.

Mercaptan - An organic compound containing hydrogen, carbon, and sulfur (RSH).

Microcrystalline Wax - A non-crystalline solid hydrocarbon with a melting point of about 106 to 195°F. Also known as petrolatum.

Motor Octane Number - An octane rating determined by testing the gasoline at an engine speed of 90 rpm and thus a better indicator of high-speed performance.

Naphtha - A petroleum fraction including parts of the boiling range of gasoline and kerosine, from which solvents are obtained.

Octane - The numerical rating of a gasoline's resistance to engine knock.

Olefins - Unsaturated straight-chain hydrocarbon compounds seldom present in crude oil, but frequently in cracking processes.

Overhead Accumulator- A tank in which the condensed vapors from the tops of the fractionators, steam strippers or stabilizers are collected.

Paraffin Wax - A crystalline solid hydrocarbon with a melting point of 105 to 155°F.

Petroleum - A complex liquid mixture of hydrocarbons and small quantities of nitrogen, sulfur, and oxygen.

Raffinate - The oil-rich solution formed during the solvent refining extraction step.

Raw - Untreated or unprocessed.

Reduced Crude - The thick, dark, high-boiling residue remaining after crude oil has undergone atmospheric and/or vacuum fractionation.

Research Octane Number - An octane rating determined by testing the gasoline at an engine speed of 60 rpm.

Sour - Denotes the presence of sulfur compounds such as sulfides and mercaptans that cause bad odors.

Spent Caustic - Aqueous solution of sodium hydroxide that has been used to remove sulfides, mercaptans, and organic acids from petroleum fractions.

Stabilizer - A type of fractionator used ro remove dissolved gaseous hydrocarbons from liquid hydrocarbon products.

Stripper - A unit in which certain components are removed from a liquid hydrocarbon mixture by passing a gas, usually steam, through the mixture.

Sweet - Denotes the absence of odor-causing sulfur compounds such as sulfides and mercaptans.

Topping Plant - A refinery whose processing is largely confined to oil into raw products by simple atmospheric distillation.

Waste Loading - Total amount of a pollutant substance, generally expressed as pounds per day.

ABBREVIATIONS

API - American Petroleum Institute

bbl - barrel

BOD - Biochemical Oxygen Demand

bpcd - barrels per calendar day

bpsd - barrels per stream day (operating day)

BS and W - Bottom Sediment and Water

COD - Chemical Oxygen Demand

lb/day - pounds per day

LPG - liquefied petroleum gas

mgd - million gallons per day

mg/L - milligrams per liter (parts per million)

psia - pounds per square inch, absolute

psig - pounds per square inch, gauge (above 14.7 psia)

RSH - mercaptan

scf - standard cubic feet of gas at 60°F. and 14.7 psia

SS - suspended solids

VSS - volatile suspended solids

APPENDIX D

INTERPRETATION OF WATER QUALITY PARAMETERS

GENERAL

The quality of a stream is generally defined in terms of its physical, chemical, biological, and bacteriological characteristics. The degree of degradation of quality is interpreted as the extent to which the existing conditions depart from specified desirable levels. The specified levels have been established to provide safeguards against nuisances or harm to plant and animal life. Water quality is usually expressed in terms of parameters that are measurable by standard analyses. An interpretation and discussion of the important water quality parameters follows.

ACIDITY

Acidity is not a specific polluting substance but rather a combined effect of several substances and conditions. It may be defined as the power of a water to neutralize hydroxyl ions, and it is expressed in terms of the calcium carbonate equivalent of the hydroxyl ions neutralized. Acidity is usually caused by the presence of free carbon dioxide, sulfuric and other mineral acids, weakly-dissociated acids, such as phosphoric, that affect the buffering action, and salts of strong acids and weak bases.

No limit has been recommended for acidity in drinking water standards.

ALKALINITY

Like acidity, alkalinity is not a direct or specific pollutant, but it is rather a measure of the effect of a combination of substances and conditions in water. By definition it is a measure of the power of a solution to neutralize hydrogen ions and it is expressed in terms of an equivalent of amount of calcium carbonate. Alkalinity is caused by the presence of carbonates, bicarbonates, hydroxides, and to a lesser extent by borates, silicates, phosphates, and organic substances.

No limits for alkalinity have been recommended in the drinking water standards, but a concentration of 20 mg/L has been recommended for unaerated water to inhibit corrosion.

BACTERIA

For many years the best available indicator of the sanitary quality of water has been an estimate of the density of coliform bacteria. The results of this test are not specific in that many bacteria common to the soil are included. Therefore many health agencies have not been satisfied with criteria based on this test. More recently tests have been developed for the determination of fecal coliforms and fecal streptococci which are attributable to human or animal sources. However, sufficient information has not been developed to apply the results of these tests. Until criteria are developed which are more specific, many states have retained the widely used coliform test.

At best, this method measures indirectly the quantitative presence of bacteriological contaminants. While only certain types of coliform bacteria are associated with pathogens, an excessive amount of coliform organisms would indicate a potentially undesirable level of pathogenic bacteria.

The Tennessee Valley Authority has suggested the adoption of criteria based on fecal coliform organisms to provide a more direct method of limiting disease-producing organisms.

COLOR

Color in water may be of natural, mineral, or vegetable origin, caused by metallic salts, humus material, peat, tannins, algae, weeds, and protoza. Waters may also be colored by soluble inorganic or organic wastes from many industries including mining, refining, pulp and paper, chemicals, and others. The term "apparent color" is used for colors that include an effect from suspended matter. The unit of color considered as a standard is the color produced by the platinum-cobalt method, and results are conventionally expressed as units of color.

The USPHS drinking water standards limit the color of acceptable water to 15 units.

FOAM

Foam or froth in watercourses is unsightly. Foams are generally created by agitation or aeration of surface-active agents, such as detergents. Detergents are refractory compounds in that they are decomposed very slowly by biological processes. Detergents inhibit oxygen transfer in biological wastewater treatment processes, increase turbidity, interfere with coagulation, and sometimes produce taste or odor. Detergents are not toxic to fish in the concentrations normally found in watercourses; however, a maximum permissible concentration of alkylbenzene sulfonate of 0.5 mg/L has been established. This limit appears to have been based on aesthetic rather than toxicological considerations.

NUTRIENTS

The presence of even trace amounts of nutrients such as phosphates, ammonia and nitrates in surface waters encourage the growth of plants such as algae in water. Where these substances are present in greater amounts, they often trigger abundant growths of such plants. Large growths of algae are unsightly, often interfere with swimming, boating and water skiing, impart tastes and odors to water, and when they die in the early fall they add a substantial organic load to the stream often causing depletion of dissolved oxygen. Significant sources of nutrients are sewage effluents, certain industrial wastes, and land runoff particularly from farm lands.

For drinking water the U. S. Public Health Service has established the maximum limit for nitrate at 10 mg/L as N. No limits have been established for ammonia or phosphates. In fact ammonia is frequently used along with chlorine for the disinfection of public water supplies.

Of the three nutrients only ammonia may exert a toxic effect on aquatic life. This effect is usually more pronounced at higher pH values. Precise limitations must be determined from a toxicological study for a particular stream and given species of fish. For the control of algae the suggested limitation for elemental phosphorus has been set by a number of researches at 0.03 mg/L.

OIL

Oily substances can be deleterious in domestic water supplies. The potential effects are:

1) Production of taste and odors,

2) Presence of turbidity, film, or iridescence,

3) Increased difficulty of water treatment, with possible hazard to the health of consumers.

Free oil and emulsions may act on the gills of fish to interfere with respiration, and they may coat and destroy algae and other plankton thereby removing a source of fish food. Settleable oily substances may coat the bottom, destroy benthal organisms, and interfere with spawning areas. Soluble and emulsified materials ingested by fish can taint the flavor of the flesh. Organic materials may deoxygenate the waters sufficiently to kill fish. Water-soluble components may exert a direct toxic action on fish or fish food. Oil film can interfere with the natural processes of stream reaeration and photosynthesis if thick films of free oil are present.

If the depth of contamination of the water surface is assumed to be 1 inch, the following table indicates the significance of oil contamination.

Appearance	Concentration mg/L	Gallons of Oil per sq. mile of surface
No visible sign of oil	6	Less than 25
Barely visible under good light	15	25
Silvery Sheen	30	50
Traces of color	60	100
Bright bands of color	120	200
Dull Color	400	666
Dark Color	800	1,332

These data indicate that oil pollution should not be visible if the amount of contamination does not exceed 10 mg/L, but when it increases to about 20 mg/L, visible identification may be expected. The effluent criteria for oil should probably be less than 20 mg/L in the effluent, with the river water quality being about 1 to 2 mg/L.

Oil Analyses - Analyses for oily materials are performed according to the American Petroleum Institute (API) method, which involves the extraction of oily substances from a sample of wastewater with carbon tetrachloride followed by an infra-red spectro-photometric analysis. A standard calibration curve is developed for SAE 20 motor oil, and all values are expressed as mg/L of oil. Substances which are extracted by the carbon tetrachloride and have a molecular weight higher than motor oil will yield low concentration as oil. Conversely, those compounds of lower molecular weight will yield higher concentrations as oil.

Oil STS Analyses - The API method for oil STS (Susceptibility to Separation) is a procedure for determining the feasibility of removing suspended oil from effluent wastewater by means of gravity-differential separation. This analysis involves the determination of oily substances in a sample which has been allowed to settle for 30 minutes. The units are expressed as mg/L of oil and indicates the amount of oil which cannot be removed by gravity separation.

OXYGEN DEMAND

For most water uses, an ample amount of dissolved oxygen is desirable. However, water with zero dissolved oxygen would be desirable as a means of inhibiting corrosion, especially in industrial cooling waters. Low concentration of dissolved oxyen may contribute to an unfavorable environment for fish and other aquatic life, and the absence of dissolved oxygen may give rise to obnoxious odors resulting from anaerobic decomposition. Low dissolved oxygen values in surface waters may result from the presence of oxygen-demanding organic substances, an inorganic chemical oxygen demand, and increased water temperature. Significant sources of organic substances are sanitary sewage, organic industrial wastes, and in some instances, decaying plants and leaves.

Biochemical Oxygen Demand (BOD) - Indicates the amount of oxygen required for biological oxidation of organic matter. The standard BOD analysis is based upon a five-day oxidation of the sample. A biological oxidation of sewage normally takes twenty days for completion, and this 20 day BOD by definition is an ultimate BOD. The BOD_5 value is approximately 68 percent of the ultimate BOD value. The COD and ultimate BOD of a pure organic substance are theoroetically the same. However, some organic compounds, such as acetic acid, are difficult to oxidize chemically, while others, such as cellulose and elemental carbon are biologically inert but do exert a COD. The BOD_5 of untreated municipal sewage is approximately 200 mg/L.

Chemical Oxygen Demand (COD) - indicates the amount of oxygen required for chemical oxidation of organic and other oxidizable materials. The COD of untreated municipal sewage normally is about 300 mg/L.

pH

pH is defined as the logarithm of the reciprocal of the hydrogen ion concentration and is expressed in units ranging from zero (0) to fourteen (14). Low values indicate the presence of acids or acid-forming salts. High values indicate the presence of alkaline material. A pH of 7.0 is considered neutral. High pH values in streams are often the results of excessive utilization by algae of the free (CO_3) and half-bound carbonates (HCO_3) in natural waters.

Although the U. S. Public Health Service drinking water standards specify no limits of pH, extreme values are to be avoided because of effects on treatment processes, piping and many industrial processes. In streams and water courses, the most significant effect of extreme values of pH is the possible lethal effect on fish and other aquatic life. pH values in the 5.0-9.0 range are generally acceptable.

REFRACTORY COMPOUNDS

Refractory compounds are defined herein as those that resist ordinary water or wastewater treatment. Refractory compounds are primarily organic. The main effects are development of taste and odor, and increase of oxygen demand. If a compound cannot be removed in a normal biological treatment system, it will be discharged to a receiving watercourse and exert an oxygen demand downstream. Refractory compounds can also cause taste and odor in drinking water supply because the standard water treatment methods will not remove them. While phenol is considered the classic contributor to tastes and odors, it can be biologically degraded in a wastewater treatment system. The U. S. Public Health Service has identified over 12 compounds which because of their refractory nature are major taste and odor producers. These compounds are: Tetralin, Acetophenone, Bis-(2-chloroethyl) ether, 2-Ethylhexanol, Dissobutyl carbinol, Bis-(21chloroisopropyl) ether, -Methylbenzyl alcohol, Naphthalene, 2-Methyl-5-ethyl pyridine, Ethylbenzene, Styrene, and Isophorone.

SOLIDS

Solids can be detrimental to fish and aquatic life. They can settle to the stream bed destroying food organisms or damaging fish-spawning beds. Solids can trap bacteria and organic wastes on the bottom and promote anaerobic decomposition. Solids can cause turbidity, which will interfere with the penetration of light, thus restricting photosynthesis and making it more difficult for fish to locate food. Excessive turbidity interferes with the feeding habits and retards the growth of certain types of shell fish.

Solids in water are classified as either "dissolved" (capable of passing a fine mat of asbestos fiber in a Gooch crucible), or "suspended" (retained on the asbestos mat). Both dissolved and suspended solids may be differentiated further as "fixed" (inorganic) and "volatile" (organic materials, or volatile matter driven off by ignition at about 600°C). Total suspended solids include solids which are floatable, settleable, or truly suspended (non-separable).

Dissolved solids indicate the total amount of inorganic chemicals in solution. The major portion of the dissolved solids are the carbonates, bicarbonates, sulfates and chlorides of sodium and calcium. All of these salts can be leached from the soils or geological deposits and are therefore present in the natural waters. Significant amounts of these chemicals are also found in sewage and industrial effluents. Land runoff, water treatment sludges and industrial wastes discharged after treatment with lime are major sources of carbonates. Likewise chlorides are leached from the soil, and found in the discharge of human waste, brines, and industrial wastes, as well as street washings. Sulfates are of natural, as well as industrial, origin.

Excessive dissolved solids are objectionable to waters used for public or industrial water supply. In public water supply, they may be objectionable from a public health standpoint. In an industrial water supply they may lead to scaling, foaming or accelerated corrosion.

The U.S.P.H.S. drinking water standards recommend a limit of 500 mg/L of total dissolved solids.

TASTES AND ODORS

Discharges of untreated as well as treated sewage, digester liquors, industrial wastes, algae and decaying vegetation, as well as land runoff contribute significant tastes and odors to surface waters. Accidental spills of organic chemicals have been also found to be a source of objectionable tastes and odors. Odor is usually measured in terms of the number of volumes of odor-free water that is necessary to add to a sample until the odor is just detectable. This number is referred to as the threshold-odor number.

A recent analytical technique has been developed for measuring taste and odor producing compounds. The technique is Carbon Chloroform Extract (CCE), and it involves absorption of materials on activated carbon followed by extraction of the carbon with chloroform. The extract is dried and the residue is expressed as mg L of CCE. The 1962 Drinking Water Standards set a recommended limit of 0.2 mg/L CCE based on studies by the U.S.P.H.S.

Phenol

Phenolic compounds may affect fish by exerting a direct toxic action and by imparting a taste to the fish flesh. There is a wide spectrum of toxic levels and considerable overlap between the lethal or damaging concentrations and those that do not harm fish in specified time periods.

The toxicity of phenol toward fish increases as the dissolved oxygen concentration is diminished, as the temperature is raised, and as the hardness is lessened. Phenol appears to be less toxic toward fish food organisms and other lower aquatic life than toward fish. Phenolic compounds in minute quantities in domestic water supplies impart distinctive taste and odors. Chlorination greatly magnifies the taste and odor characteristics.

The U. S. Public Health Service drinking water standards limit the concentration of phenolic compounds to 0.001 mg/L. The levels accepted for fish and aquatic life are approximately 0.2 mg/L. The allowable effluent quality criteria can be expected to be less than 0.1 mg/L.

Sulfide

Sulfides are constituents of many industrial wastes, and are also generated in sewage and some natural waters by the anaerobic decomposition of organic matter. When added to water, soluble sulfide salts such as sodium sulfide (Na_2S) dissociate into sulfide ions, which in turn react with a hydrogen ion in the water to form HS- or H_2S, the proportion of each depending upon the resulting pH value. When reference is made to sulfides in water, the sulfide is probably in the form of HS- or H_2S.

The toxicity of solutions of sulfides to fish increases as the pH value is lowered. However, inorganic sulfides have proved fatal to sensitive fishes such as trout at concentrations between 0.5 and 1.0 mg/L as sulfide, even in neutral and somewhat alkaline alkaline solution.

Sulfides impart unpleasant taste and odor to drinking water. The threshold odor has been reported as low as 0.2 mg/L of sulfides. Most water quality criteria do not list specfic concentrations for sulfides.

TEMPERATURE

Water temperature is important in terms of its effect on aquatic life, the use of water for cooling purposes, and its influence on the self-purification processes in a stream. Increased temperatures reduce the solubility of oxygen in water. With respect to fish, higher temperatures increase metabolism and respriation and thus require more oxygen. High temperatures have also been reported to intensify the effect of toxic substances. Increased water temperature speeds biological degradation processes and thus accelerates the demand on the oxygen resources of the stream. This in turn upgrades the treatment needed to maintain the required dissolved oxygen levels. A temperature of 95°F is about the maximum acceptable for aquatic life. The optimum range of temperatures for biological waste treatment systems is 86-95°F.

TOXICITY

General

Most quality criteria refer to toxic substances and attempt to establish specific guidelines. Although much research has been done with respect to the toxicity of specific ions to plants and animals, the number of variables involved in setting limits for aquatic or human life is too great to provide a definite limiting value for each ion or possible combinations of ions. Thus, toxicological evaluations of materials involve inductive techniques and predict only a range of levels which may have an effect upon the species tested. To be meaningful, toxicity studies require considerable time, serious conscientious investigation, and highly competent interpretation of the results.

The research being conducted on toxicity is constantly providing up-to-date information concerning the toxicity of the substances to various forms of plant and animal life. A normal procedure involved in specifying levels of toxicants is usually based upon incorporating a safety factor into the median tolerance limit of the test animals.

Cyanide

The toxicity of cyanides toward fish is affected by the pH, temperature, dissolved oxygen, and concentration of minerals. The toxicity of cyanide is also increased at elevated temperatures, a rise of 10°C producing a two t~ three-fold increase in the rate of lethal action. Toward lower organisms, cyanide does not appear to be as toxic as toward fish.

The WHO International and WHO European Drinking Water Standards both set a maximum allowable limit of 0.01 mg/L for cyanides, as CH-. In 1962, the U.S.P.H.S. Drinking Water Standards set a recommended limit of 0.01 mg/L and a mandatory limit of 0.2 mg/L.

The toxicities of cyanides toward fish have been reported to range from 0.05 to 0.15 mg/L. The allowable effluent criteria can be expected to be less than 0.1 mg/L.

Metals

Dissolved metallic ions create turbidity and discoloration, can precipitate to form bottom sludges, and can impart taste to waters. However, limits on metals are usually based on toxicity levels. The more common metals will be discussed.

The toxicity of copper to aquatic organisms varies signigicantly with the species, and also with the physical and chemical characteristics of the water, such as, temperature, hardness, turbidity and carbon dioxide content. Copper concentrations ranging from 0.015 to 3.0 mg/L have been reported as toxic to many kinds of fish and other aquatic life. Copper can also be detrimental to biological waste treatment systems. The U.S.P.H.S. drinking water standards recommend a limit of 1.0 mg/L. Limits of 0.02 mg/L have been recommended for fish in fresh water and 0.05 mg/L for fish in sea water. The allowable effluent quality criteria will probably be less than 0.05 mg/L.

Cadmium acts synergistically with other substances to increase toxicity. Cadmium can form a complex with cyanide in metal plating wastes; but in dilute solutions the complex is almost completely dissociated and highly toxic. Synergism of the toxic cadmium and cyanide ions liberated in the dissociation is indicated. The 1962 Drinking Water Standards of the U.S.P.H.S. set a mandatory limit of 0.01 mg/L for cadmium and the WHO European Standards prescribe a tolerance limit of 0.05 mg/L. The lethal concentration for fish varies from about 0.01 to about 10 mg/L depending on the test animal, the type of water, temperature, and time of exposure. The allowable effluent quality criterion would probably be less than 1.0 mg/L

Chromium is picked up by plants from the soil, and is toxic at all concentrations. The chromate ion is slightly more toxic than the chromic ion at equivalent concentrations. The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synerglistic or antagonistic effects, especially that of hardness. There appears to be no evidence that hexavalent chromium is more toxic toward fish than the trivalent form. The U.S.P.H.S. Drinking Water Standards of 1962 set a mandatory limit of 0.05 mg/L for hexavalent chromium. Allowable effluent criteria can be expected to be less than 1.0 mg/L.

Dissolved iron in excessive amounts adds an objectionable color to water and stains plumbing fixtures. In the presence of alkalinity, it reacts to form an insoluble salt which settles to the stream bed. In sufficient amounts, these solids may smother the eggs of fish. In slightly buffered streams the above reaction may lower the pH to a level which is detrimental to fish and other aquatic life. The maximum concentration of iron is listed as 0.3 mg/L in the U.S.P.H.S. Drinking Water Standards.

Nickel appears to be less toxic to fish than copper, zinc, brass, and iron. Nickel combines readily with cyanide to form a nickel-cyanide complex that is relatively stable. It can be present in water at concentrations greater than 100 mg/L as cyanide without harm to fish life if the water is moderately alkaline. In acid waters, however, the complex breaks down and releases hydrogen cyanide. The U.S.P.H.S. Drinking Water Standards do not place any limit on nickel. No data on the toxicity of nickel to man are revealed, but the toxicity is believed to be very low. Nickel is extremely toxic to citrus plants. The allowable effluent quality criterion would probably be less than 20 mg/L.

Zinc exhibits considerable toxicity towards fish and aquatic life. In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/L have been reported to be lethal. The sensitivity of fish to zinc varies with species, age and conditions of the fish, as well as with the physical and chemical characteristics of the water. The presence of copper appears to have a synergistic effect on the toxicity of zinc. The U.S.P.H.S. Drinking Water Standards of 1962 set a limit of 5 mg/L of zinc in acceptable water supplies when no alternate sources are available. The WHO International and European standards also prescribe a permissible or recommended limit of 5.0 mg/L. Zinc has no known adverse physiological effects upon man except at very high concentrations. The allowable effluent quality criterion would probably be less than 10 mg/L.

APPENDIX E

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APPENDIX F

FUNDAMENTAL PROCESSES

Introduction

For this pollution profile, twenty separate processes have been selected as the fundamental processes essential to production of final products from crude oil. The brief discussion of each fundamental process will cover: The application of the process in the overall refinery scheme; raw materials and products involved; process description; waste generated, including water, solids, air and thermal considerations; the principal subprocesses (alternative methods of carrying out the fundamental process); and related economic and technological information and trends.

The major sources for the process descriptions were the "1966 Refining Process Handbook" of Hydrocarbon Processing magazine (1) and W. L. Nelson's Petroleum Refinery Engineering (2). Information regarding the wastes from each process was obtained from ROY F. WESTON files (3), personal interviews (4), and Aqueous Wastes from Petroleum and Petrochemical Plants by W. R. Beychok (5).

Crude and Product Storage

Application: Crude oil storage is used to provide adequate supplies of feedstocks for primary fractionation runs of economical duration. Intermediate product storage equalizes flows within the refinery. Final product storage is used to store the finished products prior to shipment, to mix and blend products, and to lessen the effects on refinery operations of changes in product demands.

Charge: Crude oil or refinery products

Products: Crude oil or refinery products

Process Description: Crude oil and intermediate and finished products are stored in steel tanks ranging in size from a few thousand barrels to more than a hundred thousand barrels. Generally, operating schedules permit detention periods sufficient for settling of water and suspended solids. The settled water layer is drawn off at intervals depending on the rate of accumulation.

Wastes: Wastes associated with storage of crude oil and products are mainly in the form of free and emulsified oil and suspended solids. During storage, water and suspended solids in crude oil separate, with the water accumulating under the oil and solids forming a bottom sludge. When the water layer is drawn off, emulsified oil present at the oil-water interface and some solids are often lost to the sewers. This waste is high in COD and contains a lesser amount of BOD. Bottom sludge is removed at less frequent intervals; it is generally disposed of to landfill. Additional quantities of waste result from leaks, spills, salt "filters" (for product drying), and tank cleaning.

Intermediate storage is frequently the source of polysulfide-bearing wastewaters and iron sulfide suspended solids. Finished product storage can produce high-BOD, alkaline wastewaters, as well as tetraethyl lead. Tank cleaning can contribute large amounts of oil, COD and suspended solids, and a minor amount of BOD. Leaks, spills, open or poorly ventilated tanks, and improper landfill disposal can also be a source of air pollution, through evaporation of hydrocarbons into the atmosphere.

Trends: Many refineries now have storage tanks equipped to minimize the release of hydrocarbons to the atmosphere. This trend is expected to continue and probably accelerate. Equipment to minimize the release of hydrocarbon vapors includes tanks with floating-roof covers, pressurized tanks, and/or connections to vapor-recovery systems (6). Floating-roof covers add to the wastewater flow from storage tanks. Modern refineries impose strict Bottom Sediment and Water (BS&W) specifications on crude oil supplies, and they frequently have mixed-crude storage tanks; consequently, little or no wastewater should originate from modern crude storage. Another significant trend is toward increased use of dehydration or drying processes preceding product finishing. These processes significantly reduce the water content of finished product, thereby minimizing the quantity of wastewater from finished product storage.

Crude Desalting

Alternative Subprocesses:

1. Chemical Desalting
2. Electric Desalting - Petrolite
3. Electrical Desalting - Howe-Baker
4. Electrostatic Desalting

Application: Removal of inorganic salts and certain suspended solids from crude oil to reduce mechanical plugging in process equipment, coke formation in furnaces, and corrosion. Desalting also provides removal of arsenic and other impurities which act as poisons to catalytic cracking catalysts.

Charge: Crude oil

Products: Crude oil from which most water-soluble and solid contaminants such as chlorides, sulfates, bicarbonates, sand silt, etc., have been removed. Arsenic is also substantially reduced.

Process Description: Common to all types of desalting are an emulsifier and a settling tank. Salts can be separated from the oil by water washing in the presence of chemicals specific to the type of salts present and the nature of the crude oil. In chemical desalting, chemicals are added to the crude oil, and water is added and mixed with the crude to form an emulsion. The emulsion is heated to 150-350°F and held in a settling tank for 20-60 minutes. The salts and other impurities attach to or dissolve in the water droplets, which in turn coagulate and settle out. The desalted crude is drawn off the top of the settling tank.

The electrical methods of crude desalting differ from chemical desalting in that demulsifying chemicals are used only when the crude oil is abnormally high in suspended solids. Normally the oil is mixed with fresh water to form an emulsion. The water, which now contains most of the impurities, is separated from the oil in a settling tank under the influence of a high voltage electrostatic field, which acts to agglomerate the dispersed water droplets and accumulate them in the lower portion of the tank. The water containing the various removed impurities is continuously discharged to the wastewater system. Clean desalted crude flows from the top of the tank and is ready for subsequent refining.

Wastes: The continuous waste stream from a desalter contains emulsified and at times free oil, ammonia, phenol, and suspended solids. Ammonia is added in many refineries to reduce corrosion. These pollutants produce a relatively high BOD and COD. This waste also contains enough chlorides and other dissolved materials to contribute to the dissolved solids problem in areas where the waste is discharged to fresh water bodies. There is also a potential thermal pollution problem, because the temperature of the desalter waste often exceeds 200°F.

Trends: Electrical desalting is used much more than chemical desalting and is rapidly replacing it. In the future, chemical methods are expected to be used only as a supplement to electrical desalting where the crude oil has a very high salt content. The growth in capacity of desalting units will parallel the growth of crude oil capacity.

Crude Oil Fractionation

Alternative Subprocesses: Atmospheric Fractionation; Vacuum Fractionation; Vacuum Flashing; Crude Distillation, Three Stages.

Application: Serves as the basic refining process for the separation of crude petroleum into intermediate fractions of specified boiling point ranges.

Charge: Crude oil (desalted)

Products: A complete range of fractions including: gas, straight-run gasoline, naphtha, kerosene, diesel fuel, heating oils, cracking stock, base stocks for wax and lubricating oil, fuel oil, and asphalt.

Process Description: There are several possible combinations of fractions and quantities from crude distillations. The combination used in any particular case depends upon the type of crude being processed and the desired products. This description of crude distillation is intended to represent only one possible combination of equipment, Crude Distillation-Three Stages, which consists of:

1) an atmospheric fractionating stage which produces the lighter oils;
2) an initial vacuum stage which produces well-fractionated lubricating oil base stocks and a "long" residue for subsequent propane deasphalting;
3) a second vacuum stage designed for high vacuum, which fractionates surplus atmospheric bottoms not required or not suitable for lube production plus surplus initial vacuum-stage residuum not required for deasphalting. This third stage adds to the unit the the capability of removing catalytic cracking stock from surplus bottoms. A light ends fractionating section is included to stabilize the light straight-run gasoline.

Crude oil is heated in a heat exchanger then in a direct-fired crude charge heater. The combined vapor and liquid effluent from the heater flows to the atmospheric fractionating tower where the vaporized distillate is fractionated into a gasoline overhead product and four liquid sidestream products - naphtha, kerosene, light diesel oil, and heavy diesel oil. The overhead gasoline is condensed and pumped to a stabilizer where the gasoline is debutanized or depropanized to produce straight-run gasoline. The gas products include butane, propane and methane.

Part of the reduced crude from the bottom of the atmospheric tower is pumped through a direct-fired heater to the vacuum lube fractionator, where the distillate is separated into a gas oil and three lube oil sidestreams. Propane deasphalting feedstock is withdrawn from the bottom of the tower. The remainder of the atmospheric tower bottoms plus all of the vacuum lube fractionator bottoms not required as deasphalting feedstock are combined and charged to a third direct-fired heater. In the tower the distillate is condensed in two sections and withdrawn as two sidestreams. The two sidestreams are combined to form catalytic cracking feedstocks. An asphalt base stock is withdrawn from the bottom of the tower.

Wastes: The wastes from crude oil fractionation generally come from three sources. The first is the water drawn off from overhead accumulators prior to recirculation or transfer of the hydrocarbons to another fractionator. The water that separates from the hydrocarbons in these accumulators is drawn off and discharged to the sewer system. This water is a major source of sulfides, especially when sour crudes are being processed; it also contains significant amounts of oil, chlorides, mercaptans, and phenols.

A second significant waste source is discharge from oil sampling lines; this oil should be separable but may form emulsions in the sewer. A third possible waste source is the very stable oil emulsions formed in the barometric condensers used to create the reduced pressure in vacuum distillation units; however, when barometric condensers are replaced with surface condensers, oil vapors do not come in contact with water, and emulsions do not develop.

Trends: The general industry trend to larger and more complete refineries has been reflected also in larger and more complex crude fractionation units. Thus, the simple atmospheric "topping" units are being replaced by the atmospheric-vacuum combinations with an increasing number of sidestream products. Installed capacity now totals 3 million barrels per day. Modern refineries use surface condensers in place of barometric condensers. This reduces pollution significantly.

Thermal Cracking

Alternative Subprocesses:

1. Delayed Coking
2. Fluid Coking
3. Thermal Cracking
4. Visbreaking

Application: In this profile study the term Thermal Cracking is used to define a fundamental process that includes visbreaking, delayed coking, and fluid coking as well as regular thermal cracking. Heavy Oil fractions are broken down into lighter fractions by application of heat and pressure but without the use of a catalyst. With regular thermal cracking there is a minimum of gasoline production but more middle distillate and stable fuel oils. Visbreaking or coking maximizes the production of catalytic cracking feedstocks and thus indirectly increases gasoline production.

Charge: Reduced crudes, asphalts, and unfractionated crudes.

Products: Coke, fuel oils, gas oil, naphtha, gasoline, and gases.

Process Description: Basic to all thermal cracking processes are a furnace where the feed is heated to cracking temperatures and a fractionator where the cracked products are separated. The heat breaks the bonds holding the large molecules together, and under certain conditions some of the resulting smaller molecules may recombine to give molecules even larger than those in the feedstock. The products of this second reaction may be again decomposed into smaller molecules depending on the time they are held at cracking temperatures.

Visbreaking is a mild form of thermal cracking; it causes very little reduction in boiling point, but significantly lowers the viscosity of the feed. The feed is heated and cracked slightly in a furnace. The furnace effluent is then quenched with light gas oil and flashed in the bottom of a fractionator. Gas, gasoline, and furnace oil fractions are drawn off, and the heavier fractions are recycled.

Coking is a severe form of thermal cracking in which the feed is held at a high cracking temperature long enough for coke to form and settle out. The cracked products are sent to a fractionator where gas, gasoline, and gas oil are separated and drawn off. The heavier materials are recycled to the coking operation.

Wastes: The major source of wastes in thermal cracking is the overhead accumulator on the fractionator, where water is separated from the hydrocarbon vapor and sent to the sewer system. This water usually contains various oil fractions and may be high in BOD, COD, ammonia, phenol, and sulfides. The waste has an alkaline pH and may have a high alkalinity.

Trends: Visbreaking and coking are the two major forms of thermal cracking in the U. S. today. The older forms of thermal cracking, which were significant before the introduction of catalytic cracking, have been practically eliminated. Increasing use of visbreaking and coking will largely compensate for the downtrend of these older methods.

Catalytic Cracking

Alternative Subprocesses:

Fluid Catalytic Cracking - UOP
Fluid Catalytic Cracking, Model IV
Fluid Catalytic Cracking, Orthoflow
Fluid Catalytic Cracking, Two Stage
Houdriflow
Houdry - Fixed Bed

Application: To increase the yield and quality of gasoline and other desirable products while minimizing the yield of residual fuels.

Charge: Naphthas, gas oils, coker distillates, deasphalted oils, and sometimes unfractionated crude oil.

Products: High-octane gasoline, diesel oil, furnace oil, olefins, isobutane, butane and dry gas.

Process Description: The major parts of a catalytic cracking unit are the reactor, regenerator, and fractionator. Catalytic cracking does essentially the same thing as thermal cracking, but the presence of a catalyst permits operation at lower temperatures and pressures, thus giving greater yields of high-octane gasoline. The process involves at least four types of reactions: 1) thermal decomposition; 2) primary catalytic reactions at the catalyst surface; 3) secondary catalytic reactions between the primary products; and 4) removal of polymerizable products from further reaction by adsorption on the surface of the catalyst as coke. This last reaction is the key to catalytic cracking, because it allows decomposition reactions to move closer to completion than is possible in thermal cracking.

Cracking catalysts include synthetic silica-alumina, natural silica-alumina, treated bentonite clay, fuller's earth, aluminum hydrosilicates, and bauxite. These catalysts are in the form of beads, pellets, and powder, and are used in a fixed bed, in a moving bed, or in fluidized form. Fluidized catalyst is finely-powdered material which has the essential physical characteristics of a fluid and is transferred as such. The various modifications of fluid catalytic cracking account for most of the catalytic cracking capacity in the U.S.

In a fluid catalytic cracking unit, finely powdered catalyst is lifted into the reactor area by the incoming oil feed which immediately vaporizes upon contact with the hot catalyst. Vapors from the reactor pass upward through a cyclone separator which removes most of the entrained catalyst. The vapors then enter the fractionator, where the desired products are removed and heavier fractions recycled to the reactor. Spent catalyst passes downward through a steam stripper and into the regenerator where the carbon deposit is burned off. The regenerated catalyst again mixes with the incoming charge stream to repeat the cycle.

Wastes: Catalytic cracking units are one of the largest sources of sour waters in a refinery. Pollution from catalytic cracking generally comes from the steam strippers and overhead accumulators on fractionators used to recover and separate the various hydrocarbon fractions produced in the catalytic reactors. The major pollutants resulting from catalytic cracking operations are oil, sulfides, phenols, and ammonia. These pollutants produce an alkaline wastewater with high BOD and COD concentrations. Sulfide and Phenol concentrations in the wastewater vary with the type of crude oil being processed, but at times are significant.

Regeneration of spent catalyst may produce enough carbon monoxide to constitute an air pollution problem. Frequently the off gases are burned in a CO boiler to prevent the air pollution problem and at the same time recover heat.

Trends: Because of the great demand for high-octane gasoline, catalytic cracking capacity is expected to continue growing at a rate faster than crude feed capacity. In 1965 fresh feed capacity increased 0.3 percent, whereas gasoline capacity increased 1.6 percent. The trend in subprocesses is greater use of fluid catalytic cracking in preference to moving or fixed-bed cracking. From 1955 to 1965 fluid catalytic cracking's share of U.S. catalytic cracking capacity increased from 72 to 82 percent (7). There is also a trend to larger fluid catalytic cracking units.

Hydrocracking

Alternative Subprocesses:

BASF - IFP Hydrocracking
H - Oil
Isomax
Unicracking - JHC
H-G Hydrocracking
Shell
Gulf Hydrocracking
Ultracracking

Application: Conversion of hydrocarbon feedstocks including distillates, gas oils, and residues into gasoline, high quality middle distillates, LPG, or low-sulfur residual fuel. The process is used to improve overall refinery efficiency and flexibility.

Charge: A wide range of feedstocks including distillates, gas oils, heavy sour crudes, and atmospheric and vacuum residues.

Products: Gasoline, high-octane isoparaffins, jet fuels, diesel fuels, and low-sulfur fuel oil. Except for gases, final products from hydrocracking do not have to be "sweetened", as they are already free of sulfur compounds.

Process Description: Hydrocracking is basically catalytic cracking in the presence of hydrogen. Because hydrogen is present, the olefins formed during cracking are saturated before they can contribute to coke formation.

Hydrocracking temperatures range from 400° to 800°F., which is lower than the temperature required in catalytic cracking. Pressures, however, are much higher in a hydrocracking unit, ranging from about 100 to 2,000 psig. Actual operating conditions and the amount of hydrogen consumption depend greatly upon the feedstock and the degree of hydrogenation desired.

The reactor effluent passes through a separator, stabilizer, and a product fractionator. Hydrogen gas is recycled from the separator to the reactor. Products from the fractionator heavier than those desired are also recycled to the reactor.

Wastes: This is a new process, and no definite information concerning its waste production has been published. At least one waste stream from the process should be high in sulfides because hydrocracking reduces the sulfur content of the material being cracked. Most of the sulfides are probably in the gas products, which are sent to a treating unit for removal and/or recovery of H_2S. However, in the product separation and fractionation units following the hydrocracking reactor, some of the H_2S will dissolve in the water being collected. This water from the separator and fractionator will probably be high in sulfides, and possibly phenols and ammonia.

Trends: Hydrocracking is perhaps the most important refinery innovation of the decade, primarily because of the flexibility it provides. It allows refineries to adjust their operations economically to meet changing market demands. Because of this, hydrocracking capacity is growing at a rapid rate. At the beginning of 1966 U. S. capacity was 117,000 bpsd. By 1968, it is estimated that total installed capacity will be approximately 400,000 bpsd.

Reforming

Alternative Subprocesses:

Catalytic Reforming - Kellogg
Catalytic Reforming - Engelhard
Houdriforming
Iso-Plus Houdriforming

Platforming
Powerforming
Thermal Reforming
Ultraforming

Application: Reforming converts naphthas to finished high-octane gasoline and produces aromatics for petrochemicals or aviation gasoline; it improves gasoline quality, but does not contribute to increased yield.

Charge: Straight-run naphthas, cracked naphthas, heavy gasoline, and naphthene-rich stocks.

Products: High-octane gasoline; benzene, toluene, xylene, and other aromatics; and isobutane. Hydrogen is a significant by-product of the process.

Process Description: Platforming is the most widely used reforming subprocess. A typical Platforming unit may be divided into three parts: the reactor heater section, in which the charge plus recycle gas is heated and passed over the catalyst in a series of reactors; the separator drum, in which the reactor effluent is separated into gas and liquid streams, the gas being compressed for recycling; and the stabilizer section, in which the separated liquid is stabilized to the desired vapor pressure. The predominant reaction during reforming is the dehydrogenation of naphthenes. Important secondary reactions are the isomerization and dehydrocyclization of paraffins. All three of these reactions result in products with higher octane ratings than the reactants. Since the reactions occur over a single catalyst, the catalyst has a dual function. It must posses an acid characteristic to promote isomerization and an electron-deficient structure to promote dehydrogenation. Platinum and molybdenum are the most widely used catalysts, with platinum predominating because it gives better octane yields. Because platinum catalysts are poisoned by arsenic, sulfur and nitrogen compounds, feedstocks usually are hydrotreated before being charged to the reforming unit.

After pretreatment the feedstock in most reforming units is combined with hydrogen-rich recycle gas. The mixture then flows through 3 or 4 reactors in series each preceded by a fired heater. The effluent from the last reactor is cooled and passes to the separator drum. The liquid from the separator drum is stabilized, and the stripped hydrogen gas is compressed and recycled to the first reactor. The catalyst in each reactor is regenerated periodically either by taking the whole reforming unit off stream or by regenerating one reactor at a time with flow continuing through the remaining reactors. In some cases a "swing" reactor is provided to replace the reactor being regenerated.

Wastes: Reforming is a relatively clean process. The volume of waste flow is small, and none of the waste streams has high concentrations of significant pollutants. The waste is alkaline, and the major pollutant is sulfide from the overhead accumulator on the stripping tower used to remove light hydrocarbon fractions from the reactor effluent. The overhead accumulator catches any water that may be contained in the hydrocarbon vapors. In addition to sulfides, the waste contains small amounts of ammonia, mercaptans and oil.

Trends: Reforming capacity in the U. S. is growing at about the same rate as total crude capacity. Reforming capacity is about 20 percent of crude capacity or approximately 1,999,000 barrels per calendar day (bpcd). In 1965 reforming capacity was 41 percent of gasoline demand, and it is estimated that this relationship will remain relatively constant.

Polymerization

Alternative Subprocesses:

1. Bulk Acid Polymerization
2. Solid Phosphoric Acid Condensation
3. Sulfuric Acid Polymerization
4. Thermal Polymerization

Application: To convert olefin feedstocks into higher-octane polymer gasoline.

Charge: All types of olefin feeds.

Products: Polymer gasoline, propane, and butane.

Process Description: Polymerization units generally consist of a feed treatment section, a reactor, an acid removal section, and a stabilizer. The feed must be treated to protect the catalyst present in the reactor. A caustic scrubber is used to remove H_2S and mercaptans, and a water wash is used to remove nitrogen compounds and residual caustic. Thermal polymerization, which is not widely used, is the only type of polymerization that doesn't use a catalyst.

After pretreatment the hydrocarbon feed is brought into contact with an acid catalyst in the reactor. The catalyst is usually phosphoric acid, although sulfuric acid is used in some older methods. The acid catalyst can be a liquid without supporting materials, a thin film on quartz, or impregnated in a solid. The effluent from the reactor is treated to remove all traces of acid from the polymerized products, in order to protect the stabilizer from corrosion and to conserve the catalyst. In the polymerization reaction two olefin molecules are joined to form a larger molecule. This reaction in the presence of a catalyst occurs at a temperature of 300-435°F and a pressure of 150-1200 psig. The temperature and pressure vary with the subprocess used. The reaction is exothermic, and the reactor temperature is controlled by using cooling water or injecting cold feed into the reactor.

Wastes: This is a rather dirty process in terms of pollution loading per barrel of charged material, but because of the small polymerization capacity in most refineries, the total waste production from the process is small. Even though the process makes use of acid catalysts, the waste stream is alkaline, because the acid catalyst in most of the subprocesses is recycled, and any remaining acid is removed by caustic washing. Most of the waste material comes from the pretreatment of the feedstock to the reactor. The waste is high in sulfides, mercaptans, and ammonia. These materials are removed from the feedstock in caustic scrubbers and wash water towers. Spent catalyst is removed periodically and causes acid and solids disposal problems.

Trends: Polymer gasoline does not have an octane rating sufficiently higher than the gasoline base stocks to be of much help in the continuing competitive market for high octane gasoline. Furthermore, the yield per unit of olefin feed is much less than alkylation yield for the same feed. Polymerization capacity in U. S. refineries has been dropping for several years and the downtrend is expected to continue.

Alkylation

Alternative Subprocesses:

1. Cascade Sulfuric Acid Alkylation
2. DIP Alkylation (Aluminum Chloride Alkylation)
3. Effluent Refrigeration Alkylation
4. HF Alkylation
5. HF Alkylation, Perco

Application: For conversion of normally gaseous hydrocarbons to high-octane motor fuel.

Charge: Isoparaffins (usually iso-butane) and olefins such as propylene, butylene, and amylene.

Products: High-octane alkylate for use as a gasoline blending component; propane and butane.

Process Description: Alkylation is the reaction of an olefin with an aromatic or paraffinic hydrocarbon, and could be considered a petrochemical process rather than a refinery process. The alkylation reaction occurs in the presence of a catalyst at carefully controlled temperatures and pressures. The catalyst, temperature, and pressure all vary with the subprocess used. The reactor products go to a catalyst recovery section, where the catalyst is separated from the hydrocarbons and recirculated to the reactor. The hydrocarbon stream is passed through a caustic and water wash before going to the fractionation section. Isobutane is recirculated to the reactor feed, and the alkylate is drawn off from the bottom of the debutanizer.

Three different catalysts, aluminum chloride, sulfuric acid, and hydrofluoric acid, are presently in use. The aluminum chloride catalyst is used in the form of a hydrocarbon complex. When aluminum chloride is used, reactor temperatures are maintained at about 120°F. If sulfuric acid is used as the catalyst, the reactor temperature is maintained at 34-40°F by refrigeration equipment. With hydrofluoric acid higher temperatures are technically feasible, but octane rating specifications generally require operation at temperatures below 70°F.

Wastes: There are three general sources of waste in a sulfuric acid alkylation unit: the overhead accumulators in the fractionation section; the alkylation reactor; and the caustic wash. Water drawn off from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but is not a major source of waste in this subprocess. The waste from the reactor consists of spent acids, and generally has a pH of less than 3; this acid stream seldom enters the sewer system because most refineries process it to recover clean acids, use it as is for neutralization, or sell it. Occasionally some leakage to the sewer does occur. The major contaminants entering the sewer from a sulfuric acid alkylation unit are generally spent caustics from the neutralization of the hydrocarbon stream leaving the alkylation reactor.

Hydrofluoric acid alkylation units do not have a spent acid or spent caustic waste stream. Any leaks or spills that involve loss of fluorides constitute a serious and difficult pollution problem. Formation of fluosilicates has also caused line plugging and similar problems. The major sources of waste material are the overhead accumulators on the fractionators.

Trends: Alkylation is replacing polymerization as the means of converting olefins to gasoline, because alkylation produces higher yields of gasoline per unit of olefin feed, and because the gasoline obtained has a higher octane rating. Alkylation capacity can be expected to continue growing as long as the demand for high octane gasoline is increasing.

Isomerization

Alternative Subprocesses:

1. Isomerate
2. Liquid phase Isomerization
3. Butamer, Penex
4. Pentafining, Butomerate
5. Catalytic Isomerization
6. Isomerization (BP), Light Naphtha Isomerization

Application: Isomerization is another processing technique available for obtaining higher octane motor fuel by converting the light gasoline materials into their higher octane isomers. An indirect route to higher octane is the use of the process to convert normal butane into isobutane needed for alkylation. To date the greatest application of isomerization is for the production of isobutane.

Raw Materials: The raw materials consist primarily of normal butane, and normal pentane and normal hexane from light straight-run gasoline. Other sources of pentane and hexane are light straight-run naphthas, natural gasoline, light catalytic reformate, and hydro-treated light naphtha from thermal cracking, coking or visbreaking units.

Products: The primary products are isobutane, isopentane, methylpentane and dimethylbutane. Isopentane has a research octane number (RON) of 92.3 as compared to 61.7 for normal pentane. The isomerate produced from most straight-run naphthas has a clear research octane number of approximately 75 compared to 25 for normal hexane. The octane numbers vary depending upon the feed composition, extent of re-cycling, and degree of fractionation.

Process Description: Isomerate is a typical isomerization process. The first section in this process is an isomer splitter, which separates isoparaffins from normal paraffins. Normal paraffins are then heated, compressed and passed through an active hydrogenation catalyst, which selectively isomerizes normal pentane and normal hexane to their respective high-octane isomers. The reactants are passed through a gas-liquid separator, where the hydrogen is removed for recycling. The liquids are sent to a stabilizer, where motor fuel blending stock or synthetic isomers are removed as product. The feed preparation fractionators can be arranged for once-through or recycle operations.

The isomerization catalyst retains its high activity for a long operating period and can be regenerated in place if it is fouled due to an operational upset. When yields are computed on a volumetric basis, the ultimate yields for butane and pentane are greater than 100 percent. Although the reactions are carried out in a hydrogen atmosphere, the process neither consumes nor produces any net hydrogen. The hydrogen suppresses cracking and hydrogenates any slight amount of cracked materials which may be formed by side reactions in the process.

Wastes: No specific data are available concerning waste discharges from isomerization subprocesses, but interviews with industry personnel and a literature review indicate there are no major problems. Sulfides and ammonia are not likely to be present in the effluent. Isomerization wastes should also be low in phenolics and oxygen demand.

Trends: The need for units to isomerize normal butane into isobutane will not be as great in areas where hydrocracking is being installed. When a hydrocracker converts heavy oils into gasoline and distillate, the resulting off gas is rich in isobutane. All refiners do not believe a separate isomerization process for the light fractions of gasoline is needed, and they suggest the stock be charged along with a normal catalytic feed. Some isomerization will occur, and the loss in octane of the reformer product is compensated for by the increased quantity of material produced.

Solvent Refining

Alternative Subprocesses:

1. Furfural Refining
2. Duo-Sol
3. Phenol Extraction
4. Udex
5. Furfural Extraction of Gas Oils
6. SO_2 Extraction
7. Sulfolane Extraction
8. DMSO Extraction
9. Propane Extraction

Application: As used in this report, solvent refining refers to methods used primarily to obtain lube oil fractions or aromatics from feedstocks containing mixtures of hydrocarbons and undesirable materials such as unstable, acidic, sulfur, organo-metallic, napthenic, and/or nitrogen compounds.

Charge: A wide variety of feedstocks can be used including reduced crude, deasphalted oil, naphtha, and catalytic reformates. The feedstock varies with the subprocess and desired products.

Products: Refined oils, high-octane blending components, and high-purity aromatics.

Process Description: Solvent refining is a complicated process, even among the generally complex refining processes. It is physical in nature, with the chemical character of the various hydrocarbons remaining unchanged. The hydrocarbon mixtures are separated on the basis of their relative solubilities without specific regard to volatility. The physical properties of the solvent and the desired products govern the specific nature of each subprocess, but there are several general operations common to most of them:

1. Drying and/or deaeration of the feedstock.
2. Extraction using countercurrent solvent contacting.
3. Separation of the bulk of the solvent from the product by heating and fractionation or evaporation.
4. Removal of traces of solvent from the product by steam stripping or vacuum flashing.
5. Purification of the solvent.

Equipment required for these operations includes contact or extraction towers, fractionators, settling drums, steam strippers, gas condensers, and atmospheric and pressurized flash towers.

The Udex process for high-purity aromatics uses a mixture of glycols and water as solvent. The solvent is fed at the top of a countercurrent extraction column, and the hydrocarbon is fed at an intermediate point, with hydrocarbon reflux at the bottom. The rich solvent is taken to a stripper, where the dissolved aromatics are removed and the solvent recirculated to the extraction column. Vapors from the stripper are condensed, with the formation of two liquid phases. Part of the water phase is used to wash traces of dissolved glycols from the raffinate, and the remainder is returned to the stripper. The hydrocarbon phase from the stripper is a mixture of aromatics from which the benzene, toluene, and a mixed ethylbenzene-xylene fraction are separated by distillation.

Process flow in a lube oil solvent refining process is similar, except that the desirable lube oil fraction is in the raffinate rather than the extract stream, and solvent recovery is more complex.

Wastes: The major potential pollutants from the various solvent refining subprocesses are the solvents themselves. Many of the solvents, such as phenol, glycols, and amines, can produce a high BOD. Under ideal conditions the solvents are continually recirculated with no losses to the sewer. Unfortunately, some solvent is always lost through pump seals, flange leaks, etc. The main source of wastewater is from the bottom of fractionation towers. Oil and solvent are the major waste constituents.

Trends: Solvent extraction capacities can be expected to increase as quality requirements for all refinery products become more stringent, as the demand for lube oils grows, and as the petrochemical industry continues to require increasing quantities of aromatics.

Dewaxing

Alternative Subprocesses:

1. Solvent Dewaxing (MEK)
2. Propane Dewaxing
3. Pressing and Sweating
4. Urea Dewaxing
5. Di-Me Solvent Dewaxing (all foreign installations)

Application: Removal of wax from lube oil stocks to produce lubricants with low pour points and to recover wax for further processing.

Charge: Either virgin distillates or decarbonized residual stocks of practically any viscosity in the raw or refined state from any crude source.

Products: Dewaxed oils with low pour points, and microcrystalline wax.

Process Description: Except for "Pressing and Sweating", dewaxing subprocesses use solvents to promote wax crystallization. The first step in "Pressing and Sweating" is to chill the waxy distillate to crystallize the wax. Most of the oil is removed by squeezing out from the wax cake when the crystallized wax is pressed. After pressing, the wax cakes are slowly heated and sweated, during which the remaining oil drains from the wax crystals.

Solvent dewaxing, using methyl ethyl ketone (MEK), is the most widely used subprocess. Essential equipment in MEK dewaxing is as follows:

1. Direct-expansion ammonia chillers.
2. Double-pipe scraped-surface exchangers for solvent dewaxing and wax recrystallizing.
3. Continuous dewaxing filters.
4. Tubular exchangers to chill the wash solvent.
5. Product recovery systems.
6. Solvent-water separating and recovery systems.

In operation, the solvent is introduced into the waxy distillate stream at selected points in the chilling cycle to insure the wax crystal structure and liquid viscosity most suitable for filtration. The chilled mixture flows from the double-pipe chillers through a filter feed tank to enclosed drum-type vacuum filters. A wax-free oil filtrate is drawn through the filter cloth to tanks in which the vacuum is maintained. The wax cake deposited on the filter is washed continuously with cold solvent to produce a low oil-content wax.

The filtrate is pumped through double pipe exchangers to evaporators for recovery of the solvent. Heat for evaporating the solvent from the dewaxed oil solution may be supplied by either steam or fired heaters.

Propane dewaxing and Di-Me Solvent dewaxing are similar to the above subprocess, with propane or Di-Me Solvent being used instead of methyl ethylketone. Urea dewaxing differs in that no refrigeration is used.

Wastes: Leaks and spills are the major source of wastes in solvent dewaxing subprocesses; spillage of MEK can result in a high BOD. Propane dewaxing is a cleaner process than MEK dewaxing with respect to water pollution, but may produce some air pollution from the "smokeless" flares associated with the process.

Trends: Solvent dewaxing will completely replace pressing and sweating. Dewaxing capacity should increase as the demand for waxes and low pour point oils increases.

Hydrotreating

	Alternative Subprocesses:	Charge	Product
1.	Unifining	Cracked or Straight-Run Fractions	Feedstocks and finished products
2.	Hydrofining	Any petroleum fraction from virgin Naphthas to waxes	Feedstocks and finished products
3.	Hydrodesulfurization	Virgin or cracked naphthas, oil	Reformer feed, finished products
4.	Ultrafining	Naphtha, gas oils	Feedstocks and finished products
5.	Autofining	SR Distillates	Gasoline, kerosene
6.	Distillate Hydrogenation	Naphtha, furnace oil	Naphtha, furnace oil

	Alternative Subprocesses:	Charge	Product
7.	Ferrofining	Refined lube oil stocks	Finished lube oils
8.	Gulf HDS	High-sulfur stocks	Low sulfur fuels or cracker charge
9.	Gulf Hydrotreating	Raw Distillates or deasphalted oils	Finished gasoline-oils-waxes
10.	Gulfinishing	Solvent extracted or raw paraffinic neutral or bright stocks	Finished lube oils and waxes
11.	Selective Hydrogenation	Cracked gasoline	Finished gasoline
12.	Trickle Hydrodesulfurization	Gasoline-deasphalted oils	Cracking feeds and finished products

Application: Hydrotreating is used to saturate olefins, and to remove sulfur, nitrogen and oxygen compounds and other contaminants from either straight-run or cracked petroleum fractions.

Charge: Practically all crude oil fractions from light naphthas through waxes and lube oils. Naphthas (including gasoline) account for the largest share of hydrotreating charge stocks.

Products: Materials having low sulfur, nitrogen and olefin contents and improved stability.

Process Description: The principal difference between the many subprocesses is the catalyst; the process flow is similar for practically all the subprocesses. The most widely used hydrotreating subprocess is Unifining, which is designed to:

1) pretreat catalytic reforming feedstock;
2) improve odor, color, gum and storage stability of all distillates;
3) improve burning properties of furnace oils, cetane number of diesel fuels, and lead susceptibility of gasoline;
4) pretreat catalytic cracking feedstock.

The major equipment units in the unifining process are the reactor and the fractionator. The feed is combined with recycle hydrogen, heated to a reaction temperature, and charged to the reactor. The reactor products are cooled and enter a hydrogen separator, from which recycle hydrogen is taken overhead for return to the system. The separator bottoms flow through a low-pressure separator, where additional gases are removed, and then to a fractionator, for separation of light naphtha and hydrogen sulfide from the desirable feedstock.

The primary variables influencing hydrotreating are hydrogen partial pressure, process temperature, and contact time. An increase in hydrogen pressure gives a better removal of undesirable materials and a better rate of hydrogenation. Makeup hydrogen requirements are generally high enough to require a hydrogen production unit. Excessive temperatures increase the formation of coke, and the contact time is set to give adequate treatment without excessive hydrogen usage and/or undue coke formation. For the various hydrotreating processes the pressures range from 100 to 3000 psig. Temperatures range from less than 350°F to as high as 850°F, with most processing done in the range of 600°F to 800°F. Hydrogen consumption is usually less than 200 scf per barrel of charge.

Hydrotreating Processes can reduce the sulfur content by 80-95 percent, with the average being about 90 percent. Nitrogen usually requires more severe conditions, but reductions of 80-90 percent are feasible.

Wastes: The strength and quantity of waste depends on the subprocess used and the material being hydrotreated. Waste streams come from overhead accumulators on fractionators and steam strippers and sour water stripper bottoms. The major pollutants are sulfides and ammonia. Phenols may also be present if the boiling range of the feed is high enough.

Trends: Hydrotreating was first used on lighter materials (naphthas), but with the accumulation of operating experience and the development of better catalysts, it has been applied to increasingly heavier petroleum fractions. Hydrotreating use is increasing because the process can be applied to almost any sour feedstock, is flexible, and eliminates contaminants of concern to refineries from an operating standpoint and to the general public from an aesthetic standpoint. Increased public pressures to reduce air and water pollution will continue to enhance the overall value of hydrotreating. Consequently, hydrotreating processes are being installed in more refineries than any other process except hydrocracking.

Deasphalting

Alternative Subprocesses: Propane Deasphalting, Deasphalting and Fractionation, Solvent Decarbonizing

Application: Propane deasphalting separates asphalts or resins from viscous hydrocarbon fractions; it can be modified to segregate heavy or medium neutral fractions by extraction with propane. Solvent Decarbonizing recovers paraffinic catalytic cracking stock from distillation residues, thus increasing yields of light products at the expense of heavy fuel oil.

Raw Materials: Atmospheric or vacuum reduced crude.

Products: Deasphalted or Decarbonized Oil, and Asphalt or Heavy Fuel Blending stocks.

Process Description: The major equipment includes an atmospheric deasphalting tower and separate vacuum strippers for the tower overhead and tower bottoms products. The vacuum residue and liquid propane are pumped to the deasphalting (extraction) tower at controlled rate and temperature, producing a deasphalted oil solution overhead and an asphalt bottoms product, by separation based on different solubilities in propane. The overhead and bottoms streams both of which contain propane, are processed separately. The overhead is passed through a propane evaporator and the bottoms through a flash drum, for propane removal. The propane from both steps is recycled. The two streams are then vacuum stripped for further removal of propane and other impurities.

Propane Fractionation is a two-stage extraction process identical with the above process except that an additional extraction tower and recovery system are added for each additional product stage. Propane Fractionation is usually applied to a "long" vacuum residue and produces a medium to heavy neutral fraction in addition to cyclinder bright stock and asphalt.

Wastes: No specific data is available concerning waste discharges from deasphalting processes. Indications are that no water wastes result from the actual deasphalting step, but wastewater is discharged from the overhead condensers on the steam strippers that are used to separate the asphalt, deasphalted oil, and propane. The "sour water" from the condensers probably contains small amounts of sulfides, oil and ammonia. At times spills of asphalt may occur and set up in the sewer system. If the sewer becomes blocked, the only solution is to build a new sewer.

Trends: The factors influencing the future application of deasphalting are essentially the same as for solvent refining because in many cases solvent refining feedstocks require deasphalting as a pretreatment. Thus deasphalting capacity can be expected to increase as refinery product quality requirements become more stringent, as demand for lube oils, grows, and as petrochemical aromatic feedstock requirements increase.

Drying and Sweetening

Alternative Subprocesses:

1. Copper Sweetening
2. Electrical Distillate Treating
3. Merox
4. Solutizer
5. Adsorptive Drying and Sweetening
6. Bender (Petreco Bender)
7. Distillate Treating
8. Doctor Sweetening
9. Dualayer Distillate Process
10. Electrolytic Mercaptan
11. Girbotol
12. Glycol - Amine Gas Treating
13. Inhibitor Sweetening
14. Mercapsol
15. Phosphate Desulfurization
16. Petreco Locap Gasoline Sweetner

Application: To remove sulfur compounds, including hydrogen sulfide and mercaptans; to improve color, odor, oxidation stability, and inhibitor response. Water, carbon dioxide, and other impurities are also removed in some of the subprocesses.

Charge: A few subprocesses treat sour gases, but most treat liquid distillates including gasoline, naphtha, kerosene, jet fuel, and domestic heating oils.

Products: Hydrocarbon products of reduced sulfur content and low in water and other impurities. They are suitable for blending, shipping, or further processing.

Process Description: The method used in drying and sweetening varies greatly with each particular subprocess. "Sweetening" pertains to the removal of hydrogen sulfide, mercaptans, and elemental sulfur from hydrocarbon products. These substances impart a foul odor, and mercaptans seriously decrease the octane number of gasoline by reducing the susceptibility to tetraethyl lead. Elemental sulfur in the presence of mercaptans causes corrosion.

There are three major sweetening methods:

1) oxidation of mercaptans to disulfides
2) removal of mercaptans, and
3) destruction and removal of other sulfur compounds along with mercaptans, hydrogen sulfide and sulfur

The last of these methods is desulfurization and is generally accomplished through hydrotreating.

Processes that convert mercaptans into less odoriferous disulfides include copper sweetening, Doctor Sweetening, Bender, and Merox. Mercaptans are removed completely by being dissolved and carried away in an extracting agent or by adsorption on clay. The Mercapsol and Solutizer processes dissolve mercaptans; most of the sweetening processes use solubility promoters and caustic soda. The washing solutions are regenerated by heating and stream stripping. In Adsorptive Drying and Sweetening the mercaptans, other sulfur compounds, and water are adsorbed onto clay beds. Water removal (drying) is accomplished in most of the other methods through the use of salt filters.

Except for Adsorptive Drying and Sweetening the above subprocesses rely on gravitational settling to separate the caustic or other treating solution from the product. In cases where the treating solution and product are slow to separate, Distillate Treating or Electrical Distillate Treating can be used. These subprocesses use an electric field to enhance separation of the treating solution and product.

The Girbotol and Glycol-Amine Gas Treating subprocesses are used primarily for treating sour gases. Both processes use aqueous solutions of ethanolamines to scrub the sour gases in an absorber.

Wastes: The most common waste stream from drying and sweetening operations is spent caustic. The spentcaustic is characterized as phenolic or sulfidic depending on which is present in the largest concentration. Whether the spent caustic is actually phenolic or sulfidic is mainly determined by the product stream being treated. Phenolic spent caustics contain phenol, cresols, xylenols, sulfur compounds, and some neutral oils. Sulfidic spent caustics are rich in sulfides, but do not contain any phenols. These spent caustics have very high BOD and COD.

Other waste streams from the process result from water washing of the treated product and regeneration of the treating solution such as sodium plumbite ($Na_2 PbO_2$) in Doctor Sweetening. These waste streams will contain small amounts of oil and the treating material such as sodium plumbite (or copper chloride from copper chloride sweetening).

The treating of sour gases produces a purified gas stream, and an acid gas stream rich in hydrogen sulfide. The H_2S-rich stream can be flared, burned as fuel, or processed for recovery of elemental sulfur. The ethanolamines used in treating the sour gases are continuously resued, and very little of the treating solution reaches the sewer.

Trends: As air pollution agencies increase their efforts to control sulfur emissions to the atmosphere, the restrictions on sulfur content in fuels can be expected to tighten. This will generate a strong trend to replacement of the sweetening processes by more hydrotreating (desulfurization), because hydrotreating removes almost all sulfur compounds and not just hydrogen sulfide, mercaptans, and elemental sulfur. Nevertheless, on certain feedstocks sweetening will continue to be used because it will be as effective as and more economical than hydrotreating. Those processes producing high waste loads (Doctor Sweetening, etc.) are being replaced by the lower waste-producing processes such as Bender and Merox.

Wax Manufacture

Alternative Subprocesses:

1. Wax Fractionation
2. Wax Manufacturing, MIBK

Application: For the production of waxes of low oil content.

Charge: High oil-content wax fractions directly from crude fractionation and/or waxes from dewaxing of lube oils.

Products: Paraffin and microcrystalline waxes of low oil-content, high melting point, and other properties characteristic of high-quality waxes.

Process Description: The processing steps of Wax Fractionation and Wax Manufacturing, MIBK are very much the same, and in most respects are similar to MEK Dewaxing. Each of these wax manufacture subprocesses makes use of double-pipe scraped-surface chillers, and primary and secondary rotary vacuum filters. In the most common method of wax finishing, Wax Fractionation, a mixture of the wax-bearing charge stock with a substantial amount of solvent is chilled in double-pipe scraped surface chilling equipment to a temperature suitable for the production of dewaxed oil of the desired pour point. The mixture is then filtered, and the oil-bearing solution in the wax cake is washed continuously from the wax by displacement with cold solvent. The wax cake is continuously discharged from the primary filters and heated until the wax is totally dissolved in the solvent. Additional warm solvent is mixed into the solution, and the mixture is cooled in double-pipe scraped-surface equipment to a temperature suitable for crystallization of the desired wax fractions. The recrystallized wax is then separated by means of a second filter, on which the wax receives a final wash. The wax cake from this filter is pumped to the solvent recovery system from which the solvent-free product wax is recovered. This wax may be sent to a hydrotreating unit as a finishing step. The filtrate from the second filter, containing oil and undesirable soluble wax fractions, is pumped to the solvent recovery system from which the "soft" wax is delivered to storage tanks.

Wastes: No specific data are available, but there is no reason to believe that wastes from wax finishing are a significant source of waste material. Solvents and oil enter the wastewater system mainly through leaks. If wax particles enter the sewer system, they may interfere with settling operations in the effluent treatment plant and also may clog the sewers.

Grease Manufacture

Application: For the manufacture of a wide range of lubricating greases.

Charge: Various alkali earth metal hydroxides and fatty acids for soap manufacture, together with petroleum oils, waxes, or other materials.

Products: Lubricating greases with a sodium, calcium, aluminum, lithium, or barium soap base; mixed-base or non-soap-base greases.

Process Description: The process involves accurate weight control of all feed materials, intimate mixing, rapid heating and cooling, together with milling, dehydration and deaeration, if required. The major equipment consists of an oil circulation heater, high dispersion contactor, scraper kettle, and a grease polisher.

The soap is prepared by charging the ingredients to the contactor and heating the mixture. Saponification time varies with the type of soap, but is generally between 1/2 and 2 hours. The petroleum oil and additives are mixed with the soap base either in the contactor or in a scraper kettle. Heavier greases are normally finished in a scraper kettle because of the high viscosity which prevails at finishing temperatures.

The finished grease may be packaged directly, or processed further in a grease mill and polisher, as required by the specifications of the final product.

Wastes: Only very small volumes of wastewater are discharged from a grease manufacturing process. A small amount of oil is lost to the wastewater system through leaks in pumps. The largest waste loading occurs when the batch units are washed. This results in soap and oil discharges to the sewer system.

Trends: Because of an increase in sealed grease fittings in automobiles and longer lasting greases, a slight decline in grease production is expected through 1975.

Lube Oil Finishing

Alternative Subprocesses:

1. Continuous Contact Filtration
2. Percolation Filtration
3. Hydrotreating

Application: Principally for the production of motor oils and other lubricants, but the subprocesses can also be used to finish waxes and other fractions.

Charge: Petroleum fractions in the lubricating oil range that have been solvent extracted (and possibly acid treated). Solvent-extracted stocks usually undergo dewaxing before lube oil finishing.

Products: Finished lube oils characterized by excellent color and odor. The oils are ready for blening and compounding.

Process Description: Although solvent treating eliminates most of the dark materials in lube oil stocks, it is usually necessary to further refine the lube oils by clay treatment and at times acid treatment. The subprocesses listed are methods of clay treatment. In addition to or in place of solvent, acid, and clay treating, many lube oils are treated in drying-and-sweetening or hydrotreating units.

Acid and clay treatment are used mainly to improve the color of lubricating oils. After acid treating the lube oil must be neutralized. Neutralization is usually accomplished by contact filtration, which further decolorizes the oil while neutralizing it.

In Continuous Contact Filtration the clay adsorbent is added to the oil charge and the slurry enters a pipe still heater where maximum contact temperature is obtained in a once-through operation. From the pipe still the slurry enters a stripping tower, and steam is added to facilitate the stripping action. The slurry is drawn continuously from the bottom of the tower to a vacuum filter. The filtered oil is charged to a high vacuum stripper to furnish additional product control. Percolation Filtration consists of filtering the oil through either Fuller's earth, activated bauxite, or other clay. When the filtrate no longer meets product specifications, oil flow is stopped, the bed is washed with naphtha, and the clay is conveyed to a kiln, where the carbonaceous deposits of oil and impurities are burned off prior to its return to the filter for another cycle.

Wastes: Acid treatment of lubricating oils produces acid-bearing wastes occurring as rinsewaters, sludges, and discharges from sampling, leaks, and shutdowns. The waste streams are also high in dissolved and suspended solids, sulfates, sulfonates, and stable oil emulsions. This is a very difficult waste problem.

Handling of the acid sludge can create additional problems. Some refineries burn the acid sludge as fuel. Burning the sludge produces large volumes of sulfur dioxide that can cause air pollution problems. Other refineries neutralize the sludge with alkaline wastes and discharge it to the sewer system, resulting in both organic and inorganic pollution. The best method of disposal is probably processing to recover the sulfuric acid, but this also produces a wastewater stream containing acid, sulfur compounds and emulsified oil.

Clay treatment results in only small quantities of wastewater being discharged to the sewer. Clay, free oil, and emulsified oil are the major waste constituents. However, the operation of the clay recovery kilns involves potential air pollution problems of hydrocarbon and particulate emissions. Spent clays usually are disposed of by landfill.

Trends: Acid and clay treatment of lube oils is gradually being replaced by hydrotreating methods. Acid treatment in particular is being phased out rather rapidly.

Blending and Packaging

Application: Blending is used to produce finished petroleum products meeting required specifications at the lowest possible cost. Packaging places the finished produced into containers which industries, retailers, and consumers require.

Charge: Various refinery products, and additives to improve product quality.

Products: All the products produced in a petroleum refinery.

Process Description: Finished motor and aviation gasolines are blends of straight-run and cracked gasoline, reformate, alkylate, and other components. The percentage of each of these components varies with the quality requirements of the finished gasoline. Additives are also blended in to improve the fuel. The most common additive used in gasoline is tetraethyl lead, which is added to increase resistance to engine knock. Other additives are anti-rust, anti-oxidant, and anti-icing compounds.

Diesel fuels, lubricating oils, greases, waxes, and asphalt are other major products that are blends of various refinery streams and additives. Blending is accomplished while the products are in bulk form.

Packaging puts the large volumes of products into containers that can be used by industry, wholesalers, retailers, and individual consumers. Industrial and wholesale accounts require very little packaging because most products are sold in large volumes.

Packaging for individual consumers is done both by refineries and by customers or contract packagers. Refineries tend to restrict their packaging to high-volume, strong brand-name products, such as lubricating oils.

Wastes: These are relatively clean processes because care is taken to avoid loss of product through spillage. The primary source of waste material is from the washing of railroad tank cars or tankers prior to loading finished products. These wash waters are high in emulsified oil.

Tetraethyl lead is the major additive blended into gasoline and it must be carefully handled because of its high toxicity. Sludges from finished gasoline storage tanks can contain large amounts of lead and should not be washed into the wastewater system.

Trends: Increased use of automatic proportioning facilities for product blending. Trend toward contracting out of packaging of lower-volume products that are less suitable to highly-automated operation.

Hydrogen Manufacture

Alternative Subprocesses: Partial Oxidation, Steam Reforming, Hypro.

Application: For the manufacture of the hydrogen needed for refining operations, such as hydrotreating and hydrocracking, and for petrochemical feed stocks. Hydrogen manufacture is also the source of feed stock for production of ammonia or methanol.

Charge: The primary raw materials are natural gas, refinery gas, propane, butane, etc. Heavy fuel oil can be used in the partial oxidation process.

Products: Moderate to high-purity hydrogen. A typical analysis from a steam reforming process shows 98 percent hydrogen with less than 10 parts per million of carbon dioxide.

Process Description: The most widely used subprocess is steam reforming, which utilizes refinery gases as a charge stock. The charge is purified to remove sulfur compounds that would temporarily deactivate the catalysts.

The desulfurized feedstock is mixed with superheated steam and charged to the hydrogen furnace, which consists of a vertical combustion chamber with suspended alloy tubes containing a nickel-base catalyst. On the catalyst the hydrocarbons are converted to hydrogen, carbon monoxide, and carbon dioxide. The furnace supplies the heat needed to maintain the reaction temperature.

The gases from the furnace are cooled by the addition of condensate and steam, and then passed through a converter containing a high- or low-temperature shift catalyst depending on the degree of carbon monoxide conversion desired. Carbon Dioxide and hydrogen are produced by the reaction of the monoxide with steam.

The gas mixture from the converter is cooled and passes to a hydrogen purifying system where carbon dioxide is removed by the Girbotol Process. The carbon dioxide is absorbed into the amine solution and later driven off to the atmosphere by heating the rich amine solution in the reactivator.

Since some refining processes require a minimum of carbon oxides in the product gas, the oxides are reacted with hydrogen in a methanation step. This reaction takes place in the methanator over a nickel catalyst at elevated temperatures.

Hydrocarbon impurities in the product hydrogen usually are not detrimental to the processes where this hydrogen will be used. Thus, a small amount of hydrocarbon is tolerable in the effluent gas.

Wastes: Information concerning wastes from this process are not available. However, the process appears to be a relatively clean one. In the steam reforming subprocess a potential waste source is the desulfurization unit, which is required for feedstock that has not already been desulfurized. This waste stream would contain oil, sulfur compounds, and phenol. In the partial oxidation subprocess free carbon is removed by a water wash. Carbon dioxide is discharged to the atmosphere at several points in the subprocess.

Trends: Hydrogen requirements of the rapidly growing hydrocracking and hydrotreating processes in many instances exceed the by-product hydrogen available from catalytic reforming units. This has increased the demand for separate hydrogen manufacturing units. Since hydrocracking and hydrotreating are expected to grow more rapidly than other refinery processes, the demand for hydrogen manufacturing units should continue to be strong.